THE SEDIMENTATION AND RHEOLOGICAL BEHAVIOR OF COLLOIDAL SUSPENSIONS

By

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I can do all things through Christ which strengtheneth me.
Philippians 4:13

To my mother, Gloria Coles,
no amount of thanks would ever be enough.

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THE SEDIMENTATION AND RHEOLOGICAL BEHAVIOR OF COLLOIDAL SUSPENSIONS

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The stability of colloidal suspensions depends on the colloidal force interactions between particles. These forces include Brownian motion, van der Waals attraction, electrostatic repulsion, and steric force interactions. Properties of suspensions may be characterized by spectroscopic techniques, light scattering, electrophoresis, sedimentation, rheology, and various other methods. In this work, the stability of silica suspensions is manipulated by adjusting the electrolyte concentration and by adding an adsorbing polymer (polyethylene oxide). The stability of these suspensions is investigated using time-dependent UV-visible spectrophotometry which can characterize the sedimentation behavior. In stabilizing the suspensions using an adsorbing polymer, the concentration and molecular weight of the polymer as well as the sample preparation procedure seem to play a vital role in maintaining, re-establishing, or preventing suspension stability.

If the colloidal suspensions are dilute, as in the sedimentation study, their settling behavior is predictable theoretically, and the concentration profile of the settling particles can be described as a function of time and vertical distance by an analytical expression. By studying the particle concentration as a function of time at fixed vertical positions, the average particle size can be estimated. Therefore, UV-visible spectrophotometry may also serve as a method to characterize particle size distributions.

The complex rheological behaviors of colloidal suspensions result from colloidal forces as well as from hydrodynamic interactions. The particle size distribution also plays an important role. Under a fixed physicochemical condition, the shear viscosity of an electrostatically stabilized small particle monodisperse suspension is always higher than that of a large particle monodisperse suspension since the relative thickness of the electrical double layer is larger for the small particles. For concentrated bidisperse suspensions in which two different size particles are mixed in different proportions, the viscosity of the bidisperse suspensions is lower than either one of the monodisperse suspensions. This behavior, which was investigated through a standard rheological measuring technique, is apparently associated with changes in the microstructures of the suspensions as the relative concentrations of the two particles are varied.

CHAPTER 1
COLLOIDAL INTERACTIONS AND STABILITY

Colloidal suspensions involve particles on the order of a few nanometers to a few micrometers (microns). Colloidal stability, which usually refers to stability against coagulation, flocculation, or aggregation of these particles due to a sufficiently strong repulsive mechanism that keeps the particles separated, depends on the interactions of the colloidal forces between the particles. The forces are the same as those between atoms, molecules, and ions. However, particles contain many molecules; so, the forces between them are larger and often extend over a longer range. Colloidal forces include Brownian motion, van der Waals attraction, electrostatic repulsion, and steric interactions. Other forces such as gravity and inertia are not as important in the colloidal size range.

Brownian Motion

Small particles dispersed in water are in a constant state of random motion. This motion, which can also be observed in gases, is attributed to molecular agitation so that the motion of the particles is a result of them being constantly impacted by the solvent molecules [Einstein (1920)]. The rapid fluctuations of the molecules are on time scales corresponding to molecular motion. In characterizing these fluctuations, it is assumed that Brownian forces are uncorrelated on the time scales of the particle motion and that they are random in direction and magnitude [Hinch (1975)]. To the observer, the path of

a particle undergoing Brownian motion will appear as an irregular trajectory or a random walk [Kac (1954)].

Brownian motion can be described by using a force balance so that the mean velocity and the mean square displacement of the particles can be determined [Uhlenbeck and Ornstein (1954)]. The total force on a particle can be split into two parts. The first part is a frictional force resulting from a drag exerted by the solvent, and the second part is a fluctuating force that represents the constant bombardment felt by the particle. The fluctuating force $A(t)$ is assumed to be independent of the particle velocity $\boldsymbol{u}(r,t)$, and it also varies rapidly when compared with the variations in the velocity of the particle. The Langevin equation is the equation of motion for a Brownian particle:

$$m\frac{du}{dt} = -m\beta u + A(t). \tag{1.1}$$

Since the frictional force is governed by Stokes law,

$$\beta = \frac{6\pi a\mu}{m}. \tag{1.2}$$

In Equations 1.1 and 1.2, μ is the viscosity of the surrounding fluid, and a and m are the radius and mass of the particle, respectively. When the particle also experiences an outside field of force, such as gravity, Equation 1.1 can be written as

$$\frac{du}{dt} = -\beta u + \frac{1}{m}A(t) + K(r,t), \tag{1.3}$$

where $\boldsymbol{K}(r,t)$ is the acceleration produced by the outside force.

Solutions of the Langevin equation show that the motion of the individual particles maps out a diffusion process in the bulk system; therefore, diffusion equations which govern the probability distribution of the location of the particles can be developed [Chandrasekhar (1943); McQuarrie (1976)]. On time scales that are long when compared

to the viscous relaxation, the root-mean-square displacement of the particles becomes comparable to the particle radius. Moreover, the amplitude of the motions is greater for smaller particles, and the frequency of the particle encounters determines the maximum rate of coagulation in the absence of other colloidal forces [Overbeek (1977)].

Derjaguin-Landau-Verwey-Overbeek (DLVO) Theory

Over half a century ago, a theory of colloid stability was formulated by combining attractive and repulsive terms [Derjaguin (1940a, 1940b); Derjaguin and Landau (1941); Verwey (1942, 1945); Verwey and Overbeek (1948)]. The attractive component, which decreases as an inverse power of the separation distance, is nearly independent of the electrolyte concentration in the solution. While the repulsive contribution decreases exponentially with the separation distance, it is particularly sensitive to changes in the electrolytic content of the medium. In dilute colloidal suspensions, considering only interactions between pairs of particles is usually sufficient. As the concentration of the system increases, however, it may be necessary to account for multi-particle interactions. A brief description of the contributions to the DLVO theory of colloid stability is given below.

van der Waals Attraction

These types of forces are always present between atoms or molecules, whether charged or uncharged; therefore, they play an important role in adhesion and adsorption [Absolom *et al.* (1985); Jucker *et al.* (1998)], emulsification and coalescence [Hazlett and Schechter (1988); Deshiikan and Papadopoulos (1995a, 1995b)], fluidization [Chaouki *et*

al. (1985)], selective separation and coagulation [Pugh and Kitchener (1971); Hoskins *et al.* (1998)], wetting [Esibov *et al.* (1998)], and many other processes and phenomena. As a result, many have studied the behavior and effects of these ubiquitous forces [Margenau (1939); Hirschfelder *et al.* (1952); Margenau and Kestner (1971); Israelachvili (1992)].

Although commonly referred to as dispersion forces, three distinct forces contribute to what are collectively known as "van der Waals" forces. *Orientation* forces result from the relative orientations of interacting dipoles. An induced moment in one molecule by another molecule that has a given polarizability is a result of the *induction* effect. *Dispersion* forces result in attraction between molecules when no permanent dipoles exist, i.e. between two non-polar molecules. When a non-polar molecule interacts with a polar molecule, both dispersion and induction forces occur. Except for cases involving small, highly polar molecules, dispersion forces usually dominate the induction and orientation forces since the latter depend on the presence of dipoles.

Dispersion forces originate from fluctuations in the dipole moments of molecules. Although the time-average dipole moment of a non-polar molecule is zero, at any instantaneous point in time there is a finite dipole moment due to the specific locations of the electrons. This instantaneous dipole moment generates an electric field that induces a dipole in any neutral molecule in the vicinity. The interaction between the dipole moments of the two molecules generates an attractive force when the molecules are of the same nature. So, the dispersion force can be thought of as an instantaneous force of attraction averaged over all instantaneous configurations of the electrons of the first molecule.

The force between the interacting molecules is also affected by the presence of any other bodies nearby [McLachlan (1963)]. This means that, in reality, van der Waals forces are not additive, and the total force between two or more molecules will include a term reflecting this non-additivity arising from many-body interactions. The medium also plays an important role. The force that would exist between the molecules in the absence of the medium is modified by the mere presence of the medium. Moreover, the presence of dissolved molecules may perturb the structure of the solvent and produce a solvation force [McLachlan (1965)]. The non-additivity of these forces becomes extremely important in interactions between large particles and surfaces in a medium [Israelachvili (1992)].

van der Waals forces are long-range and can be described in terms of the physical properties of the interacting molecules. Hamaker (1937) derived an expression for the van der Waals interaction potential between two identical molecules by assuming that the London-van der Waals interaction energy was inversely proportional to the sixth power of the separation distance, r, between the two molecules [London (1937)]:

$$V = -\frac{C_{vdW}}{r^6}. \tag{1.4}$$

In Equation 1.4, C_{vdW} is the constant of proportionally. By assuming only pairwise additivity of all interactions, the following relation for the van der Waals attraction energy between two spheres results (see Figure 1.1):

$$V_A = -\frac{A}{6}\left[\frac{2a^2}{R^2 - 4a^2} + \frac{2a^2}{R^2} + \ln\frac{R^2 - 4a^2}{R^2}\right]. \tag{1.5}$$

If $H << a$, Equation 1.5 can be simplified to [Overbeek (1977, 1984)]:

$$V_A = -\frac{Aa}{12H}. \tag{1.6}$$

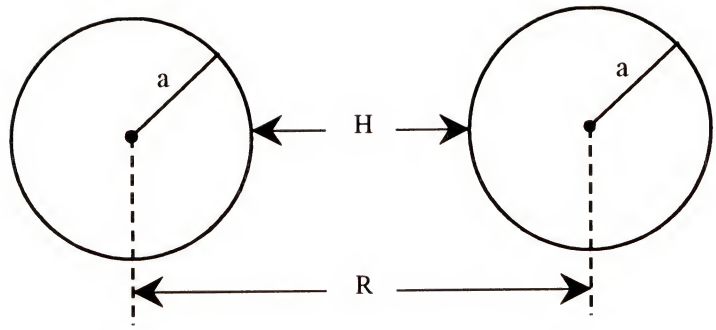

Figure 1.1 Two spheres of radius a separated by an intermolecular distance R with surface-to-surface distance $H = R - 2a$.

In the above equations, A is the well-known Hamaker constant, and it depends on the properties of the particles and the suspending medium. Typical values for A are on the order of $10^{-19} - 10^{-21}$ J.

In dilute systems, the London-van der Waals interaction energy decays even faster since the time that it takes for an electric field generated by one molecule to reach a nearby molecule and return may be on the order of the time scales on which the dipoles fluctuate. This retardation effect, which changes the power law relationship to an inverse seventh power at large distances, occurs at separations near 0.1 μm [McLachlan (1963)]. In most cases, however, only non-retarded forces need to be considered [Overbeek (1984)].

Electrostatic Repulsion

These interactions between particles result from charge formation upon suspension of the particles in a polar medium and are a direct result of ionic solution theory. The forces are most important for suspensions of particles in the colloid range, and their relative importance increases as particle size decreases.

The Debye-Huckel theory gives a theoretical foundation for the development of an expression for the range of electrostatic interactions [Hill (1986)]. In the development, the mean charge density about a central ion and the charge of that ion are opposite in sign. So, there is a tendency for ions with charge opposite to that of the central ion to distribute themselves around the central ion. The fraction of charges in a spherical shell around the central ion reaches a maximum at a distance κ^{-1} from the central ion's surface. This distance (κ^{-1}) from the central ion's surface into the solution, within which the major portion of electrical interactions with the surface can be considered to occur, is often referred to as the Debye length or the electrical double layer thickness.

In early studies, a major obstacle was the determination of the exact distribution of the counterions surrounding the central ion [Rosen (1989)]. This distribution determines the rate at which the surface potential will vary with the distance from the surface of the central ion. Early theories described the counterions either lined up parallel to the surface of the central ion or as a diffuse distribution in the solution phase near the central ion's surface. Presently, the solution side of the electrical double layer is believed to be a combination of those early theories—a layer of strongly held counterions adsorbed close to the central ion's surface on fixed sites and a diffuse layer of counterions at further distances. Thus, when two particles with distributions of counterions around their surfaces approach one another, as in a Brownian collision for example, a repulsive force results due to overlapping of their electrical double layers.

According to the model of the electrical double layer described above, the potential decreases rapidly in the first portion (the Stern layer) and decreases more

gradually in the diffuse portion. The counterions adsorbed at fixed positions near the surface of the central ion may even change the sign of the potential if there is a sufficient quantity of counterions of an adequate valence. A schematic representation of an electrical double layer is shown in Figure 1.2.

In studying the diffuse portion of the electrical double layer, κ^{-1} is viewed as an effective thickness of the ionic atmosphere [Overbeek (1982)]:

$$\kappa^{-1} = \left[\frac{\varepsilon_o \varepsilon_r RT^2}{F^2 \sum c_i z_i^2} \right]^{1/2}. \tag{1.7}$$

In Equation 1.7, κ^{-1} is a function of the dielectric constants of the medium (ε_r) and of a vacuum (ε_o), the temperature (T), and the bulk concentration (c_i) and valence (z_i) of the ions in the solution phase. (R and F are the universal gas and Faraday constants, respectively.) Since the electrical double layer thickness is inversely proportional to the charge of the solution ions and the square root of their concentrations, addition of an electrolyte will result in shorter-range electrical effects. In these cases, the electrical double layer is said to be compressed. Figure 1.3 represents the effect of electrolyte concentration on the electrical double layer thickness. The curve was obtained by using Equation 1.7 for a 1:1 electrolyte (such as NaCl) in an aqueous solvent at room temperature.

For large values of κa, the electrostatic interaction potential between two spheres is approximately [Hunter (1987)]

$$V_R = 2\pi\varepsilon_o\varepsilon_r a \psi_d^2 \ln[1 + \exp(-\kappa H)] \tag{1.8}$$

where ψ_d, the surface potential, is assumed constant. For small values of κa,

$$V_R = 2\pi\varepsilon_o\varepsilon_r a \psi_d^2 \exp(-\kappa H) \tag{1.9}$$

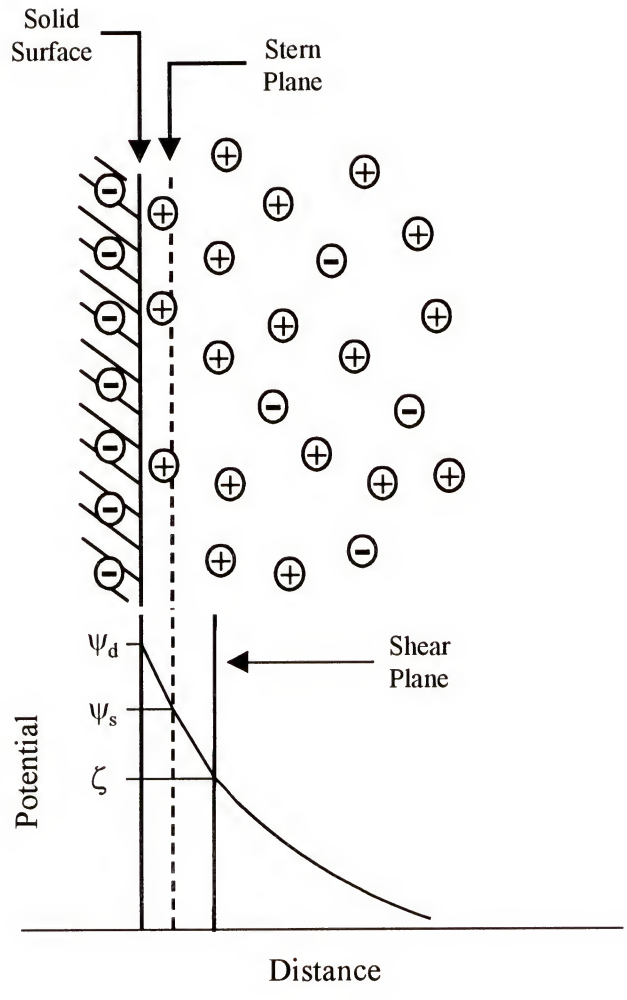

Figure 1.2 Schematic representation of the electrical double layer indicating the Stern and shear planes.

is a further approximation. Although the dependence of the electrostatic repulsion on the particle separation distance is well known, there is uncertainty in the value of the surface potential. The potential in the Stern plane (ψ_s) is often used in calculating the repulsive energy, and its nearest approximation is the zeta potential (ζ). This approximation assumes that the Stern plane and the shear plane are nearly identical.

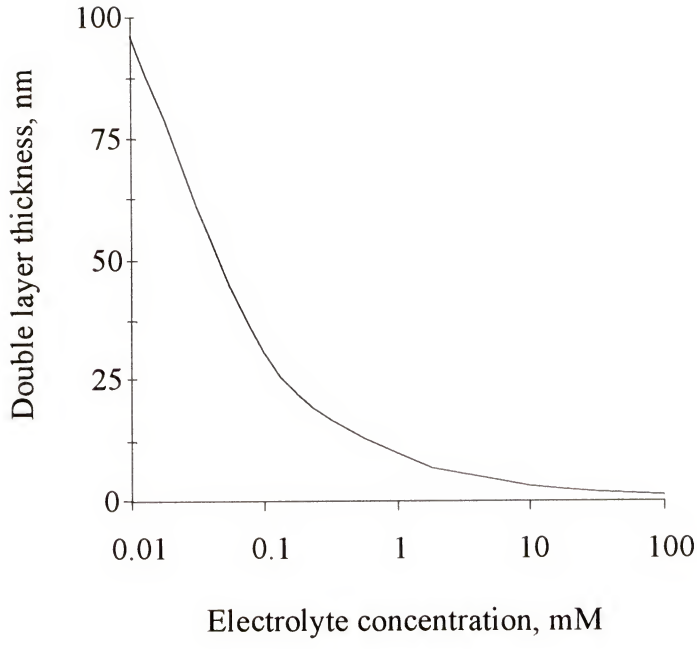

Figure 1.3 Electrical double layer thickness as a function of (1:1) electrolyte concentration in an aqueous solvent at room temperature.

Summary

By combining expressions for the van der Waals attraction (Equation 1.6) and electrostatic repulsion (Equation 1.8), a curve describing a DLVO-type interaction potential can be derived. In constructing the combined DLVO potential (V_{total}) shown in Figure 1.4, the surface potential (approximated by the zeta potential) is assumed to be 45 mV [Boersma *et al.* (1990, 1992); Okubo and Suda (1999)], and the Hamaker constant for silica interacting across water, 8.5×10^{-21} J [Lyklema (1991)], has been used. Figure 1.4 shows minima at small and large separations where van der Waals attraction dominates and a maximum at intermediate distances where electrostatic repulsion dominates. In the deep *primary minimum* that exists at small separations, two particles would be drawn together and irreversible bound to one another. In order for this to occur,

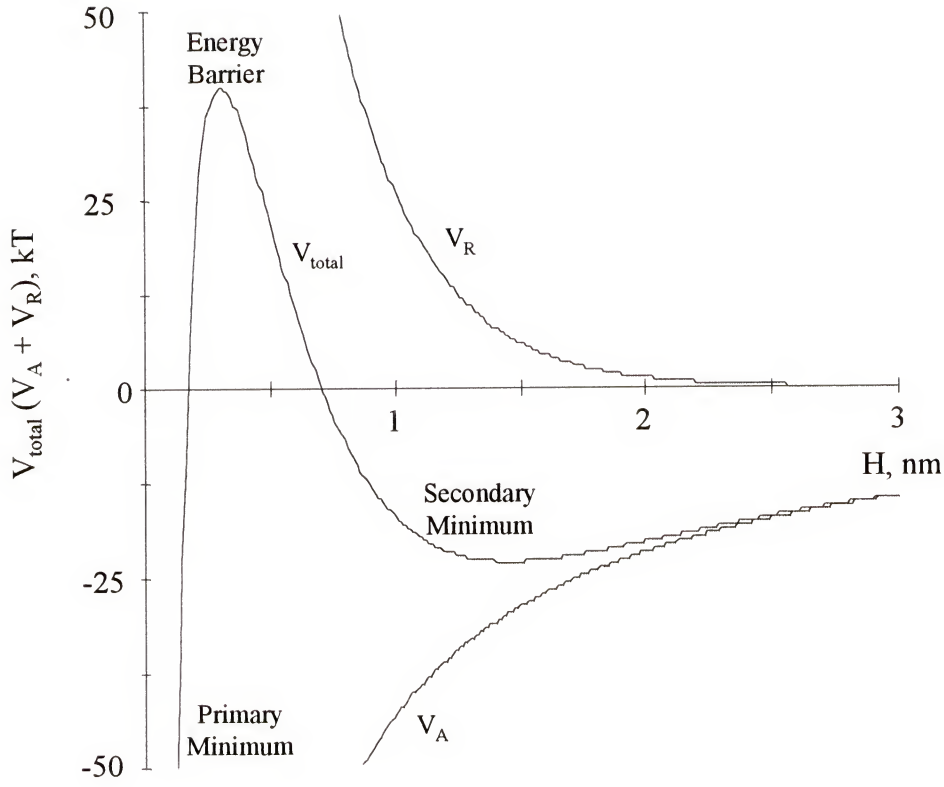

Figure 1.4 Total interaction potential (including van der Waals attraction and electrostatic repulsion) between two 0.5 μm diameter silica particles in a 10 mM 1:1 electrolyte solution (κ^{-1} = 3 nm). The surface potential (approximated by the zeta potential) is assumed to be 45 mV. The Hamaker constant is 8.5 x 10^{-21} J. V_{total} has been normalized by kT at 25 °C (4.11 x 10^{-21} J).

however, the particles would have to overcome the large *energy barrier*. Flocculation in the shallow *secondary minimum* is possible; however, it is often reversible.

The height of the energy barrier, the maximum in V_{total}, determines whether the suspension will be stable, i.e. if there will be adequate repulsion between the particles in the solution. Usually, a barrier of 10 kT (where k is Boltzmann's constant, 1.38 x 10^{-23} J/K) is considered sufficient to maintain stability [Overbeek (1977)]. High surface

potentials increase the strength of the repulsion between the particles, and low electrolyte concentrations contribute to longer-range effects.

Both van der Waals attractive and electrostatic repulsive forces can be effectively suppressed if the particles are suspended in a fluid with a refractive index nearly identical to that of the particles [de Kruif *et al.* (1985); van der Werff and de Kruif (1989); Chen and Russel (1991); Jones *et al.* (1991); Rodriguez and Kaler (1992); Shikata and Pearson (1994)]. When the refractive indices are matched, the interactions between the particles in the suspension are very small when compared to the thermal energy kT. In this case, the particles can be treated as hard spheres, i.e. non-interacting except when they are in contact.

Steric Interactions

The stability of colloidal suspensions against irreversible flocculation is often obtained by the use of powerful dispersive agents. These agents are typically various types of surfactants and macromolecules or polymers. The strength and extent of adsorption of these additives is crucial to whether the suspension will be stabilized.

Due to an Added Surfactant

The groups of chemical compounds known as surfactants are most often composed of a hydrophilic polar head group and a hydrophobic hydrocarbon chain that can be either linear or branched. The hydrophobic portion interacts weakly with the water molecules in an aqueous solvent, and dispersion force interactions between the solvent molecules force the hydrocarbon chain out of the water. However, the

hydrophilic head group interacts rather strongly via induction and orientation forces and ion-dipole interactions.

Many industrial processes such as froth flotation [Epple *et al.* (1994); Banford *et al.* (1998)], dewatering [Besra *et al.* (1998); Singh *et al.* (1998); Singh (1999)], flocculation [Somasundaran and Yu (1994)] and dispersion [Chen *et al.* (1998)], and enhanced oil recovery [Neustadter (1984); Kunieda, *et al.* (1988)] are much more efficient when surfactants are used. In solutions, surfactants can hinder the coalescence of bubbles and drops [Hodgson and Woods (1969); Keitel and Onken (1982); Li and Slattery (1988)], enhance the stability of foams and emulsions [Vincent (1984); Stoyanov *et al.* (1998)], and dramatically retard the motion of water drops [Park *et al.* (1994)].

There are a variety of interactions that may result when surfactants are added to a colloidal suspension since the polar head group may be nonionic, cationic, anionic, or zwitterionic. The nature of the surface of the particles will also determine the interparticle forces that govern the stability of a system. Therefore, surfactants play a major role in the control of the interparticle interaction forces and may either stabilize or flocculate the suspended particles, typically by adsorbing onto the particle surface.

Stabilization is often due to the formation of a protective layer of adsorbed surfactant molecules. Flocculation can be the result of bridging mechanisms caused by interactions of the hydrophobic chains adsorbed on different particles. Co-adsorption of two different types of surfactants can improve dispersions near the isoelectric point where both surfactants, when considered separately, adsorb rather poorly [Colic *et al.* (1998)]. Furthermore, the formation of mixed surfactant bilayers (see Figure 1.5) has been shown

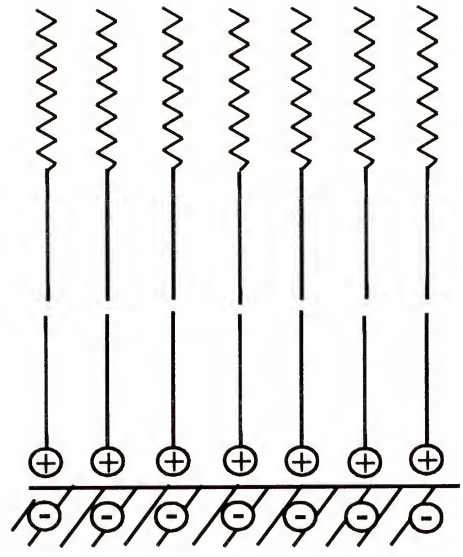

Figure 1.5 Model of a mixed surfactant bilayer adsorbed onto a negatively charged substrate.

to redisperse suspensions of previously flocculated particles through the generation of long-range steric repulsive forces [Esumi *et al.* (1990)].

Due to an Added Polymer

There have been numerous contributions to the study of suspension stability via the adsorption of a macromolecular layer. The theory was originally termed *protective action*, and the original protectors were proteins, polyelectrolytes, and gums [Napper (1983); Overbeek (1984)]. However, suitable molecules can protect nearly any material in any medium. Whether a molecule is suitable as a protector depends on the nature of its interactions with the absorbate and with the solvent. The chains must be considerably soluble in the solvent but they must also posses the ability to sufficiently adsorb onto or bind to the particle surface. Moreover, the experimental conditions are extremely important. The same polymer may cause stabilization at one condition and flocculation at another.

There are two major methods by which added polymers may adsorb onto the absorbate surface. First, polymer chains can physically adsorb onto the surface [Leong *et al.* (1995); Neuhausler and Richtering (1995); Ponton *et al.* (1996)]. Adsorption of flexible polymers onto a particle (or substrate) surface yields substantial changes in its conformational structure, and the chains usually will not collapse onto the surface due to considerable entropic losses. The final equilibrium conformation of the polymer chains, which depends on the solvent quality and polymer concentration and characteristics, resembles a random coil-like formation consisting of trains, loops, and tails (see Figure 1.6a). Trains consist of segments that are in contact with the surface. Loops contain portions of the chains in which only the initial and final segments are in contact with the surface, and tails begin at the surface but terminate in the solution phase.

A second type of adsorbed polymer molecule may possess an anchoring group of some type that can easily adsorb onto or bind to the surface of the particle [Prestidge and Tadros (1988); Inoue *et al.* (1990)]. This type of chemical adsorption, or grafting, can also be generated through polymerization reactions carried out at the surface [Laible and Hamann (1980); Liang *et al.* (1994)]. Figure 1.6b schematically illustrates this type of polymer adsorption.

When particles with adsorbed polymer molecules approach one another, they experience a force as the outer segments of the polymer chains come into close proximity. Under some conditions, the forces can be attractive, and the polymer may flocculate otherwise stable systems via a bridging mechanism. Furthermore, non-adsorbed polymer molecules may cause flocculation of a suspension due to the exclusion

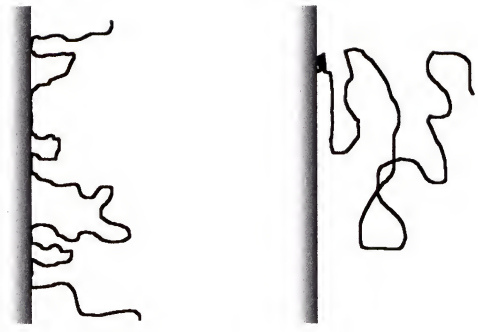

Figure 1.6 Adsorption of polymers at the solid-liquid interface.
a) Physisorption; b) Chemisorption.

of free polymer chains from within the gaps between the particles. In some cases, attractive forces are desired.

When two particles each have macromolecular layers on their surfaces, repulsive forces may also be generated. There are two different effects that often result in repulsion. As shown in Figure 1.7a, repulsion due to the restricted volume effects occurs when the extended length of the polymer chains is larger than the particle separation distance. This results in a loss of available conformations and a loss in system entropy. Furthermore, when adsorbed chains on different particles begin to overlap, there is a local increase in the concentration and in the system free energy. This osmotic effect (see Figure 1.7b) is often what is meant by the term steric repulsion/stabilization, and as a general rule, it is more important. In order for adsorption of soluble polymers in colloidal suspensions to produce a stabilizing effect, the polymer layers must prevent van der Waals forces from becoming important. If the interaction between the polymer layers is entirely repulsive, the suspension will be stable; however, purely repulsive interactions usually only occur for strongly adsorbed polymers at full coverage in a good solvent.

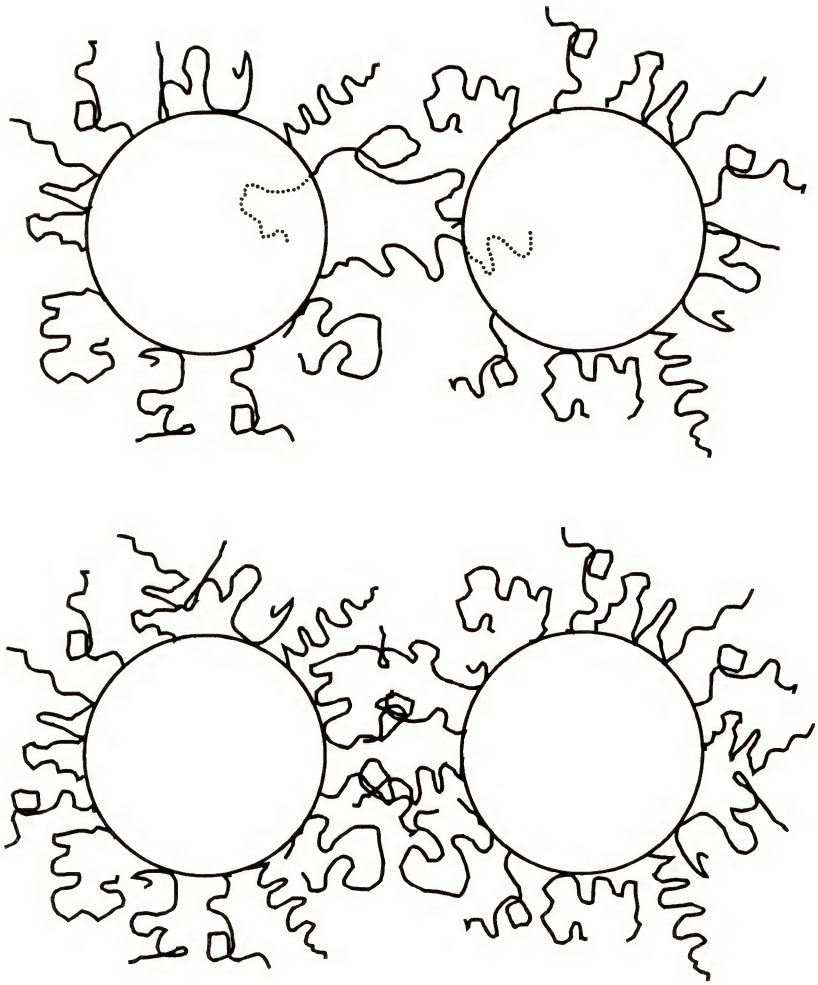

Figure 1.7 Steric repulsion between particles with adsorbed polymer chains.
a) Restricted volume effect; b) Osmotic effect.

Steric repulsion is essential to many industrial processes because suspensions of colloidal particles that would otherwise flocculate may be dispersed by addition of a suitable polymer. Moreover, polymer addition to some systems has been shown to decrease the viscosity [Zaman *et al.* (1996)]. If addition of the polymer causes a stabilization effect, the polymer behaves as a dispersant.

In early studies, steric stabilization was geared toward electrically charged particles in aqueous suspensions. Since electrostatic stabilization is not effective in non-

polar media, steric stabilization can often serve as the primary mechanism for imparting stability to such systems [de Silva *et al.* (1990a, 1990b)]. Other advantages for steric stabilization via an adsorbed polymer over electrostatic stabilization include equal effectiveness at high and low solid content and insensitivity (relatively) to the presence of electrolytes. Furthermore, sterically stabilized suspensions are thermodynamically stable whereas suspensions that are electrostatically stabilized are merely thermodynamically metastable. If polyelectrolytic macromolecules are used as steric stabilizers, however, both electrostatic and steric repulsion exists [Tadros (1980)].

Summary

The stability of suspensions ultimately depends on the interactions of the forces between the particles. In the colloidal size range, these forces are mainly Brownian motion, van der Waals attraction, electrostatic repulsion, and steric interactions due to an adsorbed surfactant or polymer layer. In order for colloidal suspensions to be stable, there must be a repulsive mechanism that counters the effects of van der Waals forces. Alone, these attractive forces lead to coagulation, flocculation, or aggregation of the dispersed phase. Stabilizing or dispersing agents may surround the particles with a repulsive cloud of counterions or provide a buffering layer of large molecules. Whatever the case, the suspension will only be considered stable in the colloidal-chemical sense when the repulsion between the particles is strong enough to keep the particles separated.

CHAPTER 2
LITERATURE REVIEW

Colloidal suspensions are used in many industrial applications. Foods, paints, inks, ceramics, and cosmetics are just a few examples [Tadros (1980); Kawaguchi (1994b)]. The suspension media can be aqueous or non-aqueous, and the suspended particles can be either organic or inorganic materials. Knowledge of the physicochemical and interaction properties of colloidal suspensions is important to understanding how they will behave during the multitude of possible processing conditions.

Characterization Techniques

Various properties of colloidal suspensions may be characterized by many different methods such as spectroscopic techniques, electrophoresis, sedimentation, and rheology. One of the most important properties of a suspension is the size of the particles. Particle size and particle size distribution yield information about the relative importance of interparticle forces, and they are necessary for interpretations of various other experimental results. Therefore, accurate information about the size of the particles in the suspension is a necessary first step to understanding many types of colloidal phenomena.

Quasielastic light scattering (QELS) and dynamic light scattering (DLS), in particular, are powerful tools that can be used to study dilute suspensions [Berne and

Pecora (1976); Bezot *et al.* (1992)]. Particle diffusion coefficients are determined and can be related to the average particle size. Multiple scattering effects that result at higher concentrations may be reduced by matching the refractive indices of the particles and the suspension medium. Fairly new methods such as two-color dynamic light scattering (TCDLS) [Phillies (1981a, 1981b); Schatzel *et al.* (1990); Segre *et al.* (1995); Overbeck *et al.* (1997); Pusey *et al.* (1997)] and fiber-optic quasielastic light scattering (FOQELS) [Berend and Richtering (1995)] have also been shown to produce good results with more concentrated suspensions by suppressing multiple scattering effects. Furthermore, commercial size distribution techniques, such as the Coulter® LS 230 Size Analyzer, can generate information rather quickly, even on fairly turbid samples.

Knowledge of the forces between particles is also considerably important in any attempt to understand the behavior of colloidal suspensions. While the DLVO theory of colloidal stability can often be applied to explain the behavior of colloidal systems, experimental verification of the colloidal forces that comprise the theory was difficult until fairly recently. The surface force apparatus (SFA) was developed by Israelachvili and Adams (1978) to measure direct interactions between two mica plates at separation distances as close as 0.1 nm and up to 100 nm. The instrument was tested in aqueous solutions of 1:1 and 1:2 electrolytes, and good agreement with DLVO theory was found at moderate separations. Similar results were also obtained by Pashley and Israelachvili (1984) at various concentrations of divalent cations. Klein and Luckham (1982, 1984a) measured the forces between two mica surfaces with and without adsorbed layers of monodisperse polyethylene oxide (MW ~ 10^4-10^5) in an aqueous electrolyte solution at a near neutral pH. In the absence of adsorbed polymer chains, the interactions were found

to be characteristic of a repulsion resulting from the overlap of electrical double layers. When PEO was adsorbed onto the mica surfaces, a repulsive (steric) interaction that monotonically increased with decreasing separation distance was observed. The repulsion was attributed to osmotic interactions that developed as the two adsorbed polymer layers began to overlap in the solvent. At low surface coverages of the polymer on the mica surfaces, long-range, reversible, time-independent attractive forces could be detected [Klein and Luckham (1982b)].

The development of the atomic force microscope (AFM) [Binnig *et al.* (1986)] allowed for the measurement of the interactions between a spherical particle and a flat surface. With this, the determination of colloidal forces on a near molecular scale was possible for the first time. Ducker *et al.* (1991, 1992) and Meagher (1992) used the technique to measure the interaction force between a silica particle and a large silica surface in aqueous electrolyte solutions at various pH values. Bowen *et al.* (1998) extended the use of the AFM to biological systems by attaching a single yeast cell to the cantilever and measuring the force distance profile between the cell and a flat mica substrate. The forces between two 2 μm diameter polystyrene spheres were measured by Li *et al.* (1993) by aligning the sphere placed on the cantilever with one chemically glued to a mica surface. Reproducible long-range repulsive forces were observed for electrolyte concentrations below 10 mM, and at 1 mM KCl, determinations of the surface potential and electrical double layer thickness reasonably agreed with expected (experimental and theoretical) values.

Total internal reflection microscopy (TIRM) was introduced [Prieve *et al.* (1987); Bike and Prieve (1990); Prieve and Frej (1990)] as a method to measure the mean

potential (as opposed to the mean force as in SFA) of the interaction between a colloidal particle and a macroscopic surface. The resolution of this technique has been shown to be better than 5 nm. Electrostatic repulsive forces, which exponentially decreased with increasing electrolyte concentration, were clearly detectable at a range of electrolyte concentrations, and gravitational forces on the order of 10 pg could be determined. Although determinations of absolute separation distances are not possible, TIRM may be applied to studying van der Waals attraction, steric interactions resulting from adsorbed polymer layers, and adhesion forces that are responsible for coagulation of particles in a secondary minimum.

Differential electrophoresis is an experimental technique that has been developed to measure the normal and tangential force holding two 5 μm diameter polystyrene latex particles, with different surface chemistries and zeta potentials, in a doublet that acts as a dipole and rotates as a rigid body when an electric field is applied [Velegol *et al.* (1996a, 1996b)]. Sugimoto *et al.* (1997) used an optical trapping technique to measure the interaction force between monodisperse polystyrene latex spheres in an aqueous solution, and their results agreed quite well with DLVO prediction at a variety of electrolyte concentrations. Three-dimensional optical trapping (3DOT) in combination with evanescent wave light scattering (EWLS) has also been employed to directly measure the interaction force between a 1.5 μm diameter silica particle and a macroscopic surface [Clapp *et al.* (1999)].

Additions of soluble macromolecules to colloidal suspensions can result in a variety of effects. If the polymer chains remain free in the system, they will have a direct bearing on the nature and strength of the forces between the particles. When the

polymers adsorb onto the surface, in addition to modifying the forces between the particles, changes in the surface properties of the particles may occur. Therefore, determinations of the adsorbed amount and bound fraction, layer density and/or layer thickness, and conformation of the adsorbed polymer chains on the particle surfaces are important for understanding the effects that the polymer addition may have on the various properties of the suspension.

Ellipsometry [Killmann (1976); Malmsten *et al.* (1992)] and Brewster angle reflectivity [Fu and Santore (1997)] can be used to measure layer density profiles of adsorbed polymers on planar surfaces and to provide information on adsorption and desorption kinetics. Often, the results obtained on macroscopic surfaces compare rather well with those on colloidal particles. For adsorption of polymers in particle suspensions, small-angle neutron scattering (SANS) has proven to be very useful in developing segment density profiles [Killmann and Sapuntzjis (1994)], determining average particle sizes [Malmsten *et al.* (1992)], and characterizing the microstructures of the suspensions [van der Werff and de Kruif (1989, 1990); Kawaguchi (1994b)]. Measurements of adsorbed amounts and specific polymer-surface interactions are possible through Fourier transform infrared spectroscopy (FTIR) [Tripp and Hair (1993)]. By using the premise that polymer segments adsorbed in trains have a lower mobility as compared with free segments in loops and tails, nuclear magnetic resonance (NMR) techniques have been used to obtain the bound fraction of adsorbed polymer layers in aqueous and non-aqueous systems by direct observation of the line widths of the polymer spectrum [Barnett *et al.* (1981); van der Beek *et al.* (1991)]. Furthermore, adsorbed polymer layer thicknesses can be determined by hydrodynamic techniques such as photon correlation spectrometry

(PCS) and ultracentrifugation (UC) [Killmann *et al.* (1985); Killmann *et al.* (1988); Lapcik *et al.* (1995)], and the thicknesses obtained are generally reasonably close to the "real" values since the effective hydrodynamic layer thickness is particularly influenced by the outer segments.

Investigation of the rheological properties of suspensions often gives insight into the stability of colloidal systems. In order for a system to be stable, a certain amount of "structure" is required. Structure within a system, by adsorption of a polymer layer for example, helps to prevent agglomeration and irreversible flocculation of particles at small separations [Tadros (1980)]. Rheological measurements are an effective means for determining the degree of structure formation in a colloidal suspension. Therefore, in order to understand the physical stability of colloidal suspensions, it is generally helpful to examine the rheological behavior.

Generally, only liquids, solutions, and very dilute suspensions exhibit Newtonian behavior. Suspensions at intermediate and high concentrations typically show non-Newtonian characteristics such as shear-thinning (pseudoplasticy) and shear-thickening (dilatancy). The suspension may even display a yield stress, and the magnitude of that yield stress may be used to gauge the strength of the interactions between the particles. Time-dependent effects such as thixotropy and rheopexy are also possible in colloidal suspensions. Figure 2.1 illustrates the shear rate dependence of shear stress and viscosity of some various flow behaviors.

The simplest type of suspension contains rigid spherical particles that only experience direct interactions upon contact. At dilute conditions, the rheological behavior of these hard spheres is simple and well understood. The viscosity dependence

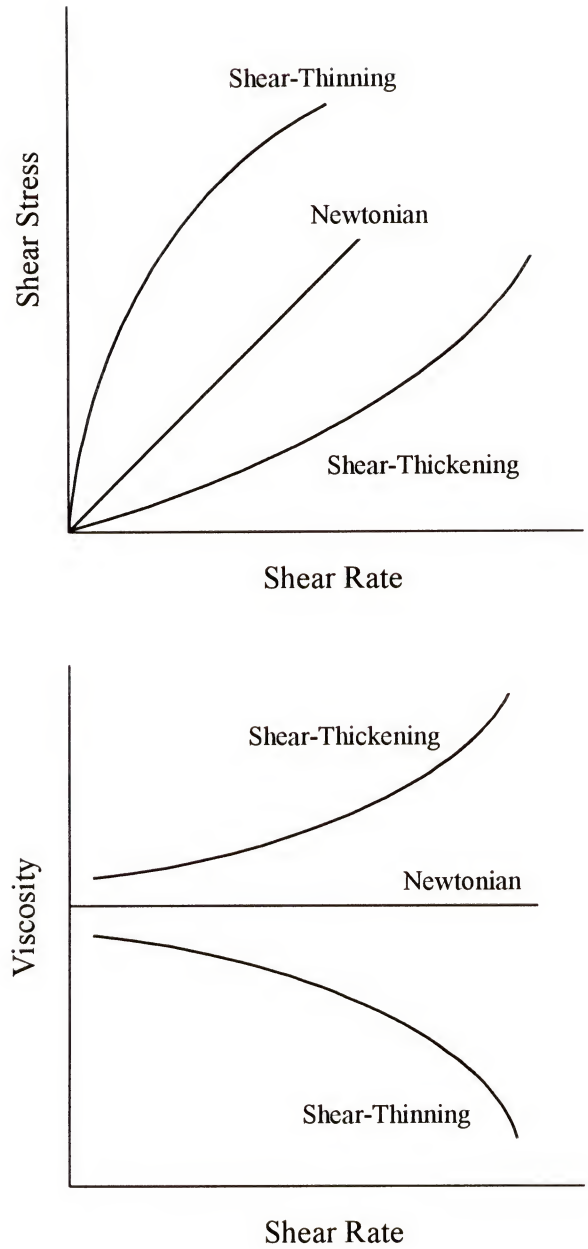

Figure 2.1 Shear rate dependence of shear stress and viscosity of some various flow behaviors.

of dilute suspensions of rigid spherical particles was first described by Einstein:

$$\eta_r = 1 + \frac{5}{2}\phi . \tag{2.1}$$

In Equation 2.1, η_r is the reduced viscosity (the viscosity of the suspension divided by the viscosity of the fluid medium), and ϕ is the volume fraction of the suspended particles. The intrinsic viscosity is defined as

$$[\eta] = \lim_{\phi \to 0} \frac{\eta_r - 1}{\phi} \quad , \tag{2.2}$$

and it is the limit of the reduced viscosity extrapolated to a zero volume fraction. For hard spheres, according to Einstein's equation, the intrinsic viscosity is 2.5.

The linear increase in reduced viscosity with volume fraction as described by Equation 2.1 does not account for the existence of charges around the particles. As the volume fraction increases, η_r increases more rapidly due to the interactions between the electrical double layers surrounding the particles [Conway and Dobry-Duclaux (1960); Krieger and Eguiluz (1976); Wagner and Klein (1991)]. The primary *electroviscous* effect is a stress that results from the distortion of the electrical double layers surrounding colloidal particles under flow conditions. The flow-induced structural rearrangement of the ions is often termed the secondary electroviscous effect. Both of these electrostatic effects serve to enhance the viscosity of a suspension as the volume fraction of the particles increases. However, they may be suppressed by addition of an electrolyte at a sufficient concentration so that the range of the electrical interactions is reduced.

Moreover, at a particular volume fraction ϕ_m known as the maximum packing volume fraction, the reduced viscosity has been shown to increase asymptotically to infinity due to the development of a rigid structure formed by the particles that ceases to flow. This phenomenon is illustrated in Figure 2.2. Hence, the dependence of reduced viscosity on particle volume fraction is very complex, particularly as ϕ increases. As a result, this relationship has been extensively studied theoretically and experimentally

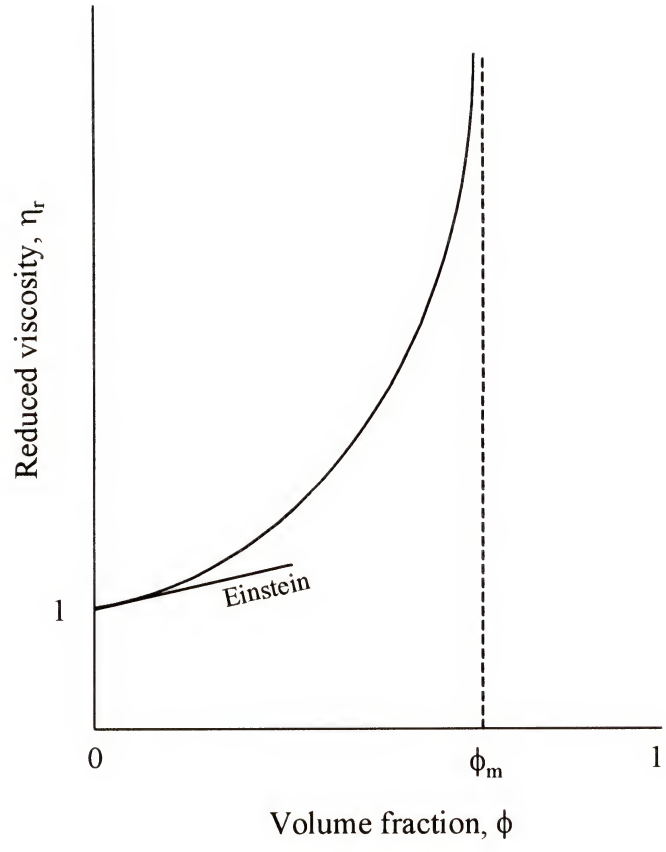

Figure 2.2 Schematic representing the dependence of reduced viscosity on particle volume fraction.

[Mooney (1951); Maron *et al.* (1951); Maron and Pierce (1956); Krieger and Dougherty (1959); Krieger (1972); Batchelor (1977); van der Werff and de Kruif (1989)].

There are two relatively simple methods that are often used to describe the reduced viscosity of a suspension as a function of the particle volume fraction. The Maron-Pierce model [Maron and Pierce (1956)] is defined as

$$\eta_r = \left[1 - \frac{\phi}{\phi_m}\right]^{-2}, \tag{2.3}$$

and the Krieger-Dougherty model [Krieger and Dougherty (1959); Krieger (1972)], which makes use of the intrinsic viscosity, is given by:

$$\eta_r = \left[1 - \frac{\phi}{\phi_m}\right]^{-[\eta]\phi_m} \quad (2.4)$$

The value for the maximum packing fraction, which depends on the particle size distribution, may be obtained by fitting either Equation 2.3 or 2.4 to experimental data.

There have also been extensive studies on the viscosity behavior of bidisperse and polydisperse suspensions [Chong *et al.* (1971); Storms *et al.* (1990); Kim and Luckham (1993); Chang and Powell (1994); Wagner and Woutersen (1994)]. In these studies, the particle size ratio and the relative volume fraction of small particles have been identified as important parameters that may be used to characterize the static and dynamic rheological behavior of a bidisperse suspension. Chong *et al.* (1971) found that their data for bidisperse suspensions of glass beads could be adequately represented by

$$\eta_r = \left[1 + 0.75\left(\frac{\phi/\phi_m}{1 - \phi/\phi_m}\right)\right]^2 \quad (2.5)$$

Equation 2.5 reduces to Equation 2.1 for dilute suspensions when ϕ_m is taken as 0.605. Storms *et al.* (1990) proposed

$$\eta_r = \left[1 + \left(\frac{R\phi}{1 - \phi/\phi_m}\right)\right]^{3.3\phi_m} \quad (2.6)$$

as an appropriate form for their studies on bidisperse suspensions of polymethyl methacrylate (PMMA) beads. In Equation 2.6, R is an empirical constant that depends on the relative volume fraction of small particles, and it was found to decrease with decreasing particle size ratio.

The rheological properties of colloidal suspensions are also affected when a polymer is added to the system [Kawaguchi (1994a); Kawaguchi *et al.* (1995)]. Steric stabilization (as described in Chapter 1), bridging flocculation, or depletion flocculation

may occur and significantly affect the rheological behavior by changing the structure of the particles in the suspensions. Steady and dynamic measurements can be used to probe the wide range of effects that may occur. Non-Newtonian shear rate dependent viscosities and time-dependent behaviors are commonly observed.

In bridging flocculation, polymer chains adsorb onto two or more particles and bind them together (see Figure 2.3). The flocs trap part of the medium within their structure, and this leads to an increase in the effective volume of the dispersed phase. Generally, a bridging mechanism occurs when the molecular weight of the polymer chains is sufficiently high and the coverage of the adsorbed polymers on the absorbate surface is rather low. In concentrated suspensions, the flocs may cease to exist as discrete entities, and above a critical concentration, the flocs may form a type of structured network. One polymer molecule may extend through many bridges when very small particles are involved. In this case, it is the particles that are adsorbed along the polymer chains [Wong *et al.* (1992)]. Otsubo (1990, 1992) studied the flocculation of silica due to a bridging mechanism and reported that the suspensions showed elastic behavior which increased with adsorbed amounts of polyacrylamide (MW ~ 10^6).

Depletion flocculation is a result of non-adsorbing polymer chains that are free in the medium. When particles approach one another, an osmotic pressure difference may develop between the spaces in between the particles and the free solution, forcing non-adsorbed polymer molecules out of the interstitial spaces. Kawaguchi *et al.* (1997) observed an increase in the storage modulus of silica suspensions upon the addition of non-adsorbing polystyrene chains. The effects were attributed to the formation of large flocs of silica particles resulting from depletion forces. Flocculation due to a depletion

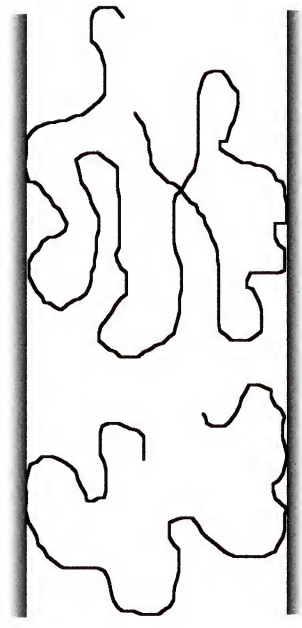

Figure 2.3 Schematic illustrating bridging flocculation between two surfaces via an adsorbed polymer.

mechanism may also be present in systems in which steric stabilization was previously established [Vincent *et al.* (1986)]. Depletion forces have also been shown to be important in bidisperse suspensions of different size particles [Xu *et al.* (1997)]. In this case, exclusion of the smaller particles, instead of non-adsorbed, coiled polymer chains, from within the interstitial spaces between the larger particles results in attractive forces.

Non-Newtonian flow behaviors are typical of colloidal suspensions, with and without added polymer chains. Kawaguchi *et al.* (1991) investigated the rheological properties of aqueous silica suspensions in the presence of adsorbed hydroxypropyl methyl cellulose (HPMC). Shear-thinning behavior was observed for slurries of the bare silica particles. At high concentrations of a 400 000 molecular weight HPMC, the silica suspensions displayed rheopectic behavior. Moreover, due to large adsorbed amounts of HPMC, there was a transition in the structure of the silica suspensions from solid-like to

liquid-like during shear, and the critical shear rate at which this transition occurred increased with the concentration of HPMC. It was proposed that the solid-like behavior of the aqueous silica suspensions was reinforced by the formation of a gell-like material, which was created with the adsorption of the HPMC.

In addition to rheological studies, there are numerous other techniques that may be used to study the stability of colloidal suspensions. Some of these methods are visual observation, turbidity, and sedimentation. Kawaguchi (1994a) estimated the stability of silica suspensions by visually observing how long they remained suspended without sedimentation after homogeneous mixing. Turbidity or optical density measurements can be used to ascertain the degree of flocculation in some systems [Long *et al.* (1973); Saunders *et al.* (1997)]. The slope of a plot of turbidity versus wavelength yields a parameter n, which is a measure of the degree of flocculation. In colloidal suspensions, n is a measure of the particle size, and it decreases as the extent of flocculation increases.

A spectrophotometer (also commonly called a spectrometer) can be used to measure the turbidity of a suspension as a function of wavelength [de Silva *et al.* (1990a)], and it can also be used to monitor the turbidity as a function of time at a fixed wavelength [Cowell *et al.* (1978); Lapcik *et al.* (1995)]. By monitoring time changes in turbidity, which may be linked to particle concentration, the sedimentation behavior of the suspension can be used to describe the stability of the system. According to Stokes law, the sedimentation velocity of a particle in a dilute suspension is given by:

$$U_S = \frac{2a^2(\rho - \rho_o)g}{9\mu}, \tag{2.7}$$

where a is the particle radius, μ is the viscosity of the fluid, g is the acceleration due to gravity, and ρ and ρ_o are the densities of the particle and fluid, respectively. From

Equation 2.7, it is clear that larger particles settle faster than smaller particles. Therefore, the coagulation of smaller particles (due to suppressed electrical double layers, bridging or depletion flocculation, etc.) resulting in the formation of larger particles will have a dramatic effect on the rate at which the suspension settles [Farley and Morel (1986)], and this sedimentation behavior can be qualitatively viewed as a measure of the stability of the suspension.

Particle size, polydispersity, and interparticle interactions are all very important in understanding the behaviors of colloidal suspensions. When polymeric molecules are added to colloidal suspensions, nearly all of the characteristics of the suspension will be effected. Depending on the nature of the polymer and its interactions with the particles in the suspension, the stability of the system may be enhanced or reduced, and the above mentioned techniques can be used to gain insight into these phenomena.

The Silica/PEO/Water System

Studies involving aqueous dispersions of inorganic oxides are of considerable practical importance [Rubio and Kitchener (1976)]. The silica/PEO/water system can serve as a model for studying the various phenomena that occur in colloidal suspensions, and consequently, this system has been explored by many researchers. Different types of silica may be used in the preparation of colloidal suspensions. They include silica powders (fumed, precipitated, Aerosil), colloidal sols, pyrogenic silica, and beads.

Silica in negatively charged at neutral pH due to dissociation of surface silanol groups [Kawaguchi (1994b)]. Since water is a well-known good solvent for PEO [Tager

et al. (1974); Ataman (1987); Vshivkov (1988)], the polymer molecules can adsorb onto the surface of aqueously dispersed silica by strong hydrogen bonds that develop between the PEO ether oxygens and the silanol groups on the silica surface [Mathur (1996)]. Furthermore, silanol groups provide good adsorption sites for PEO because they act as proton donors in the hydrogen bonding process.

At increased pH, the silica surface becomes increasingly negatively charged, and decreased adsorption of PEO results due to the reduced number of surface silanol groups available for hydrogen bonding. Moreover, at high pH values, the hydroxide ions may act as displacers, essentially lowering the effective adsorption energy of the PEO molecules. In solution, the [OH^-] may prevent the adsorption of dissolved PEO molecules, and they may also displace previously adsorbed PEO molecules [Cohen Stuart and Tamai (1988); Lafuma *et al.* (1991)]. For systems involving PEO and silica, desorption usually occurs at pH values of approximately 10.5 [van der Beek *et al.* (1991)].

Adsorption of PEO molecules onto silica particles results in changes in the surface properties and in the interparticle forces. Joppien (1978) found that adsorption of a low molecular weight PEO (20 000) significantly reduced the surface charge density of pyrogenic silica. Dynamic light scattering studies conducted by Churaev and Nikologorskaja (1991) showed that the surface charge, electrophoretic mobility, and zeta potential of silica sols with adsorbed layers of PEO (MW ~ 10^4-10^5) were much lower than the corresponding values before polymer adsorption. An adsorbed layer of a nonionic polymer like PEO on the charged silica surface may reduce the zeta potential by

shifting the position of the shear plane further away from the surface [Maier *et al.* (1987)]. In this case, no decrease in the surface potential may be observed.

The stability of colloidal silica suspensions is also effected by the addition of nonionic PEO molecules. The adsorbed macromolecules may prevent the particles from aggregating, flocculating, and/or settling, or the polymer may be effective in facilitating these unstable behaviors. Additions of PEO will also effect the rheological behavior of silica suspensions. Ponton *et al.* (1996) analyzed viscosity measurements of concentrated aqueous silica suspensions stabilized by adsorbed layers of 5000 molecular weight polyethylene oxide using a hard sphere approximation to determine the adsorbed layer thickness. The results were in good agreement with those obtained by light scattering measurements. Bridging flocculation of precipitated silica beads in the presence of a commercial grade high molecular weight ($\sim 10^6$) PEO was observed by Liu and co-workers (1994, 1996). At polymer concentrations near and above the plateau region of the adsorption isotherm, non-Newtonian shear rate dependent viscosities and time-dependent effects were reported. Moreover, sedimentation studies conducted by Killmann *et al.* (1986) revealed that the addition of a small amount of PEO to aqueous silica suspensions resulted in the formation of a "dense granular floc" that settled rapidly.

Silica suspensions provide an excellent system for studying a variety of colloidal phenomena. The surface chemistry of silica particles has been extensively studied, and the particles provide an exceptionally suitable substrate for polymer adsorption. Furthermore, polyethylene oxide, a nonionic, water soluble polymer, readily adsorbs at the silica surface by a well documented mechanism, and thus, it has been established as a model polymer that may be used to study the effects of the addition of linear, flexible,

neutral chains to aqueous colloidal systems [de Gennes (1987)]. Therefore, aqueous silica suspensions with added PEO provide and excellent model system for studying an array of adsorption phenomena.

Dissertation Organization

In this work, the stability of silica suspensions will be manipulated by adjusting the electrolyte concentration and by adding adsorbing polyethylene oxide. Time-dependent UV-visible spectrophotometry, which can characterize the sedimentation behavior, will be used to investigate the stability of the suspensions. In attempts to stabilize weakly flocculating suspensions using an adsorbing polymer, the effects of the concentration and molecular weight of the added polymer as well as the sample preparation procedure are considered. The experimental results are presented and discussed in Chapter 3. Theoretical predictions of the settling behavior of dilute colloidal suspensions are described in Chapter 4. The analysis is compared with some experimental tests and interpreted with regard to the use of the UV-visible spectrophotometer as an instrument for determining average particle size.

Appropriate techniques which address the specific issues that may arises in acquiring accurate and reproducible rheological information are often necessary; therefore, the shear viscosity behavior of concentrated monodisperse and bidisperse suspensions are studied through a standardized rheological measuring technique. The procedure, experimental results, and comparisons with published literature are given in Chapter 5. Finally, conclusions and future work suggestions are discussed in Chapter 6.

CHAPTER 3
EXPERIMENTAL SEDIMENTATION STUDIES

Materials

Silica Powder

The silica powders used for the sedimentation studies were commercially available. These high purity (>99.9%), amorphous, spherical powders were reported to have a nominal 1.0 μm diameter, a narrow size distribution, and a standard density of 2.0 g/cm^3 [Geltech (1994)]. Size distribution characterization of the powders via a Coulter® LS 230 Particle Size Analyzer confirmed their monodispersity. The results yielded an average particle size (peak value) of 1.15 μm. The BET surface area of the powders was found to be 3.25 m^2/g.

Sodium Chloride

Crystalline sodium chloride (NaCl) purchased from Fisher Scientific was used for adjusting the electrolyte concentration of the suspensions. Before use, the NaCl was heated in an oven at 105-110 °C for at least 12 hours to ensure complete evaporation of any residual water.

Polyethylene Oxide

The two polyethylene oxide (PEO) samples used were also available commercially. They were solid at room temperature. The manufacturer's catalog listed these lower molecular weight polymers as polyethylene glycol and indicated that the

polymer chains were hydroxyl-terminated at both ends [Polysciences (1998)]. Moreover, polyethylene glycol and polyethylene oxide were listed by the manufacturer as chemically identical.

Gel Permeation Chromatography (GPC) was used to determine the molecular weight distribution of the polymers. Prior to the GPC tests, the polymer samples were dried in a vacuum oven at 12 °C for one week. The experiments were performed at 35 °C with tetrahydrofuran (THF) as the solvent. A series arrangement of four polystyrene gel columns (300 mm x 4.6 mm), with pore sizes of 5×10^5, 10^4, 500, and 100 Angstroms, was used. The weight average molecular weight (M_W), number average molecular weight (M_N), and the polydispersity (M_W/M_N) obtained via GPC are shown in Table 3.1. The results shown in Table 3.1 were obtained after several months of storage. The polymer samples were stored in opaque containers, which may reduce any degradation that may occur as a result of exposure to ultraviolet (UV) light [McGary (1960)]. Since the polymer samples were relatively monodisperse, competitive adsorption effects on the equilibrium surface coverage were not considered in subsequent analyses [Dijt *et al.* (1990); Santore and Fu (1997)].

Water

Distilled deionized water was used as the suspending medium. It was observed that considerable drifts in the pH of the suspensions occurred when the water was left open to the atmosphere; therefore, immediately after distillation, the water was sealed in a container until it was needed to prepare the suspensions. Using the "sealed" water, the pH values of the suspensions were consistently between 6.5 and 7.0. This water was also used to thoroughly wash all glassware and containers prior to use.

Table 3.1 Molecular weight averages (M_W and M_N) and polydispersities (M_W/M_N) of polymer samples PEO1 and PEO2 in THF at 35 °C.

POLYMER	M_W	M_N	M_w/M_N
PEO1	13 245	11 960	1.11
PEO2	33 435	29 790	1.12

Sample Preparation Procedures

Two different sample preparation procedures were used, and they were both designed so that uniformity could be maintained from sample to sample. For both cases, the bare silica suspensions were prepared in the same manner. Silica powder was added to distilled deionized water and ultrasonicated for 4 hours. The silica was allowed to settle out and was resuspended with 1 hour of ultrasonication to verify that the particles were indeed dispersed before addition of the NaCl, PEO or NaCl/PEO solvents. The difference between the two sample preparation procedures lies in the order in which the solvents were added to the bare silica suspensions.

Ordered Addition of PEO and NaCl

Known quantities of PEO and NaCl were added to different containers of distilled deionized water, vigorously shaken, and allowed to stand overnight. To prepare PEO solvents at various concentrations, PEO solutions were mixed with distilled deionized

water in different proportions. After resuspenion of the bare silica preparations (as mentioned above), portions of the PEO solvents and the cooled bare silica suspensions were mixed to produce NaCl-free suspensions. When mixing the two solutions, the PEO solvents were always added to the bare silica. This step is essential to ensuring that the silica particles in the suspension were all exposed to the same solvent environment [Lafuma *et al.* (1991)].

Since polymer adsorption may take several hours, a macromolecule may be effective for bridging flocculation before it has had time to sufficient adsorb onto the particle surface. Therefore, it is not equivalent to add the PEO solvents to the silica preparations or to add the silica particles to the polymer solutions. In the latter case, polyethylene oxide molecules may bind to several silica particles before sufficient surface adsorption could have occurred. Therefore, the former method produces suspensions that are closer to equilibrium conditions, and this method was used throughout this work.

In order to respect the adsorption kinetics [Rubio and Kitchener (1976); Howard *et al.* (1983); Rebar and Santore (1996b)], the silica/PEO suspensions were allowed to equilibrate for at least 12 hours. Size distribution characterizations were performed after the silica/PEO suspensions were ultrasonicated for 1 hour and allowed to cool. During ultrasonication, the temperature does not exceed 40 ^{o}C; therefore, no thermal degradation of PEO should be expected to occur during this step [Madorsky and Straus (1959); Grassie and Perdomo Mendoza (1984); Calahorra *et al.* (1985); Cameron *et al.* (1989); Costa *et al.* (1992)].

After size analysis, the suspensions were diluted with distilled deionized water or a NaCl solvent. Since adsorption equilibrium of the silica particles with the added polymer should have been attained, virtually no desorption should take place upon dilution. Therefore, PEO-covered silica particles in the diluted suspension should be identical to those in the original, more concentrated suspension [Koopal *et al.* (1988)]. Again, after standing for at least 12 hours and 1 hour of ultrasonication, light absorbance sedimentation tests were conducted on the cooled, diluted suspensions.

Simultaneous Addition of PEO and NaCl

The first step in preparing these suspensions was preparation of two NaCl solutions to a desired molarity. The NaCl solutions were shaken vigorously and allowed to stand overnight. After at least 12 hours, the required amount of PEO was added to one of the NaCl solutions, vigorously shaken, and also allowed to stand overnight. To prepare the solvents, the NaCl and the NaCl/PEO solutions were mixed in different proportions to yield various PEO concentrations in the presence of NaCl.

Portions of the NaCl/PEO solvents were added to resuspended bare silica preparations. After preparing the silica suspensions with added NaCl and PEO, the solutions were shaken and allowed to stand for at least 12 hours. Prior to conducting the light absorbance tests, each silica suspension was ultrasonicated for 1 hour and allowed to cool to room temperature. In some cases, the silica suspensions with added NaCl and PEO were diluted with NaCl solutions of the final molarity so that the silica concentration could be reduced. When diluting with these NaCl solutions, the silica volume fraction decreased but the PEO to silica ratio and the electrolyte concentration remained constant.

Adsorption Equilibrium

The adsorption equilibrium of one of the polyethylene oxide samples, PEO2, on the silica particle surface was confirmed using a carbon analyzer. Solutions containing known quantities of PEO2 were added to resuspended silica preparations (as in the ordered addition sample preparation procedure) and allowed to equilibrate for at least 12 hours. During this time, the suspensions settled by gravity. After equilibrium had been reached, the suspensions were centrifuged for 10 minutes using an IEC Clinical Centrifuge, and the supernatants were removed.

Total carbon (TC) analysis of the supernatant solutions was performed, and the adsorbed amounts were determined by subtracting the equilibrium PEO2 concentration from the initial known concentration of PEO2 in the suspensions. The results indicated adsorbed amounts (Γ) of 0.3–1.4 mg/m^2 for PEO2 suspension concentrations between 4–38 ppm (2-14 mg of PEO2 per gram of silica). The data are consistent with the literature for adsorption levels in the plateau region with comparable molecular weights of polyethylene oxide in aqueous silica suspensions [Killmann *et al.* (1985); van der Beek *et al.* (1991); Malmsten *et al.* (1992); Ponton *et al.* (1996); Rebar and Santore (1996a, 1996b)]. As summary of the TC analysis for PEO2 is listed in Table 3.2.

Absorbance Tests

The intensity of light absorbed at a particular wavelength can be determined by passing a beam of light through a sample of known concentration and thickness. The

intensity of the transmitted light (I) relative to the intensity that would have been transmitted in the absence of the sample (I_o) is known as the *Transmittance*. By measuring the transmittance at different wavelengths, an absorbance spectrum can be obtained. The *Absorbance* is related to the transmittance (I/I_o) through:

$$Absorbance = \log \frac{I_o}{I}, \tag{3.1}$$

and it is directly proportional to the sample concentration (c) and thickness (d) by the Beer-Lambert law [Alberty and Silbey (1992); Perkampus (1992)]:

$$Absorbance = \varepsilon_\lambda cd\,. \tag{3.2}$$

In Equation 3.2, ε_λ is the absorbance coefficient. It is a quantity that is characteristic of the solute, and it is a function of the light wavelength (λ), the solvent, and the temperature.

The light absorbance studies in this work were conducted using a Hewlett-Packard UV-visible spectrophotometer (Model 8543). The schematics and optical path of the instrument are illustrated in Figure 3.1. The system uses two light sources, a deuterium lamp for the ultraviolet (UV) region and a tungsten lamp for the visible region. With both lamps on, the system is able to measure light absorbance spectra in the range of 190-1100 nm. All absorbance tests in this work were conducted at 500 nm (in the visible region) and at a constant temperature of 25 °C. The sample cuvettes used were made of optical glass, and had (outside) dimensions of 45 mm x 12.5 mm x 12.5 mm. The light path (or sample thickness) was 10 mm. A cuvette filled with distilled deionized water was used to obtain I_o.

Since the tungsten lamp shines through the deuterium lamp, the latter should always be ignited for accurate testing. This results in unnecessary exposure of PEO,

Table 3.2 Adsorption equilibrium of PEO2 on 1.0 μm diameter silica.

Suspension PEO2 (ppm)	Suspension PEO2 (mg/g)	Equilibrium PEO2 (ppm)	Adsorbed PEO2 (mg/m^2)
3.8	1.3	1.0	0.3
6.2	2.2	3.8	0.3
9.4	3.4	2.9	0.7
12.5	4.4	7.8	0.5
37.5	13.4	24.7	1.4

which has been shown in some studies to degrade in UV light [Rabek *et al.* (1992); Kaczmarek *et al.* (1996)], to the deuterium light source. However, the shutter only opens when actual data are being taken. Therefore, the PEO in the suspensions is only exposed to the UV light source for less than one second per measurement. This is expected to minimize any possible losses in molecular weight or changes in molecular weight distribution.

Before studying the effects of added polymer, absorbance tests were conducted to determine an electrolyte concentration necessary to sufficiently suppress the electrostatic interactions of the particles. Figure 3.2 shows absorbance vs. time data for 1.0 μm

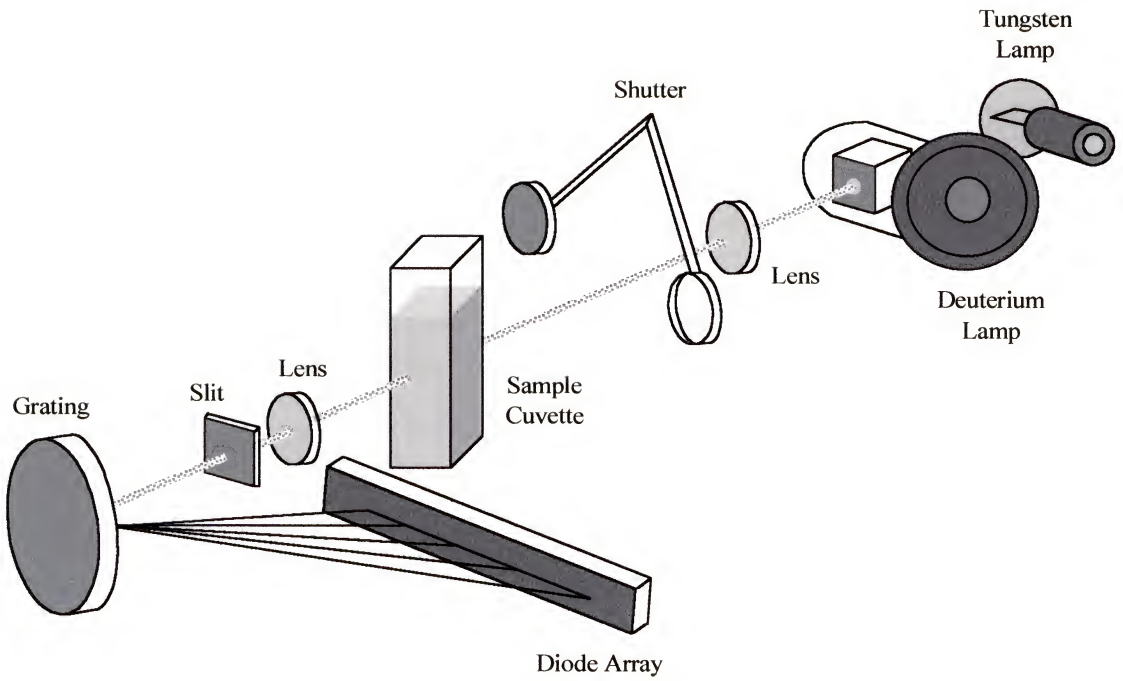

Figure 3.1 Schematic and optical path of UV-visible spectrophotometer.

diameter silica at various NaCl concentrations. The results show that up to 50 mM NaCl, the light absorbance level remains constant up to 90 min, indicating that the suspensions are stable over the testing time period. Above 50 mM NaCl, the absorbance levels begin to fall within 15 minutes. This rapid decrease in light absorbance is attributed to coagulation and fast settling of the particles as a result of compressed double layers.

Taking the results shown in Figure 3.2 into consideration, NaCl concentrations of 60-150 mM were used to destabilize the silica suspensions. Addition of PEO will be used to overcome the lack of electrostatic interactions and sterically stabilize the suspensions. At high electrolyte concentrations, it is possible for the particles to coagulate in the secondary minimum of the interaction potential or to irreversibly bind together in the primary minimum (see Figure 1.4). At the electrolyte concentrations that

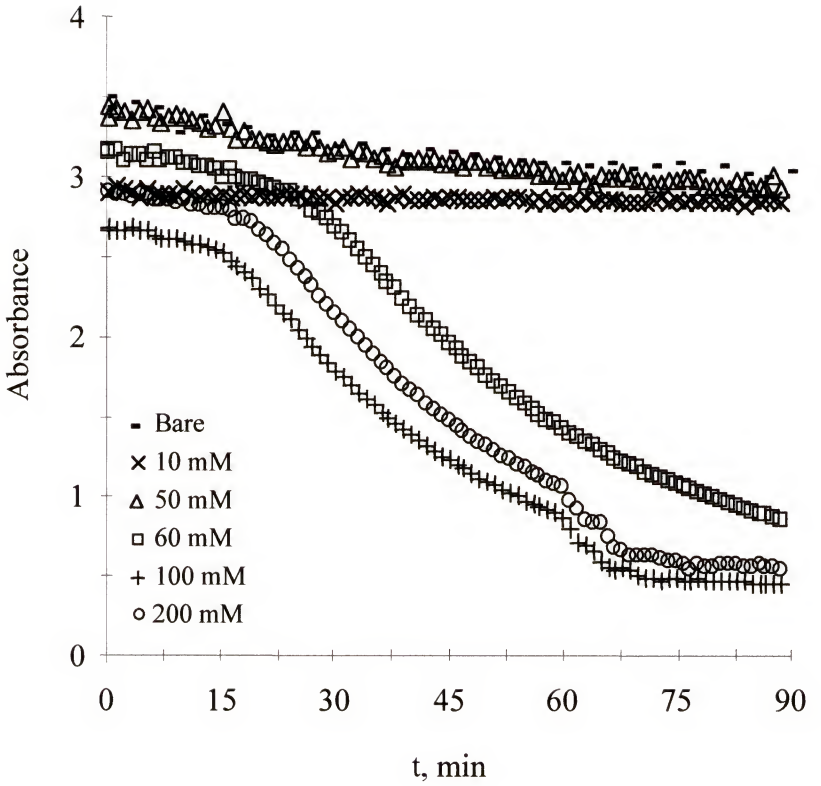

Figure 3.2 Time-dependent settling behavior at various NaCl concentrations. 1.0 μm diameter silica. $\phi = 0.07\%$.

will be considered in this work, it is desired that the addition of PEO should be capable of resuspending the particles. Therefore, the range of electrolyte concentrations used should not cause more than coagulation in the secondary minimum, i.e. the suspensions should be weakly flocculating.

Figure 3.3 is an example of the type of systems we wish to consider in this work. Time-dependent light absorbance tests were conducted after the suspension was initially prepared and after a 30 day time interval. For the second test (after 30 days), the sample was again ultrasonicated for 1 hour and allowed to cool to room temperature prior to the absorbance test. The results shown in Figure 3.3 for 1.0 μm diameter silica with 60 mM

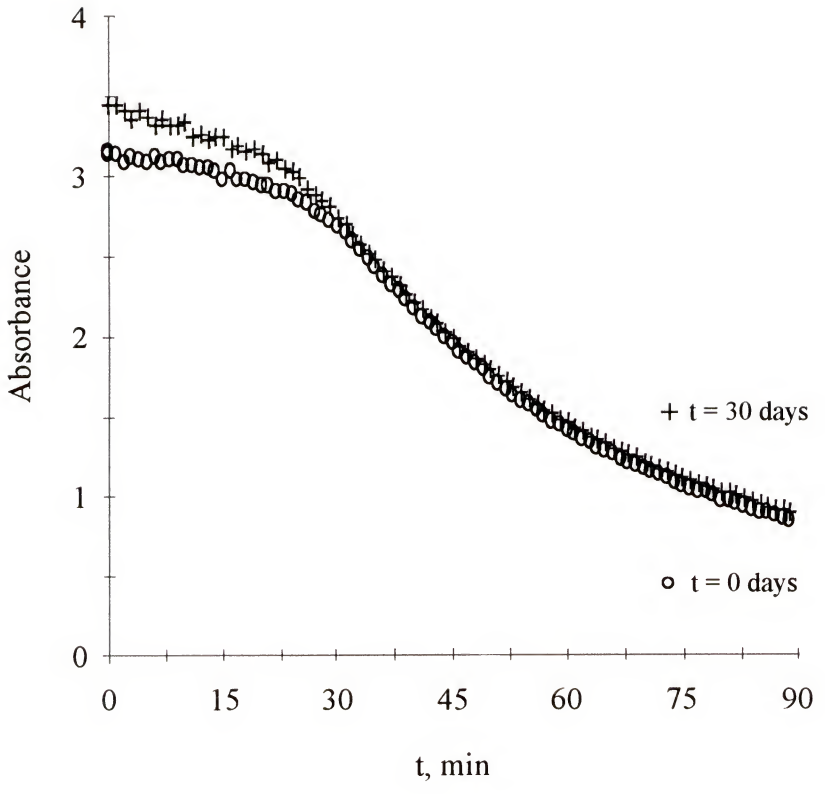

Figure 3.3 Time-dependent settling behavior indicating a weakly flocculating system. 1.0 μm diameter silica. $\phi = 0.07\%$. [NaCl] = 60 mM.

NaCl indicate that the settling behavior of the silica suspensions with added NaCl is that of a weakly flocculating system, i.e. capable of being resuspended. Moreover, the results in Figure 3.3, which also show that the absorbance tests are reproducible, are typical for the range of electrolyte concentrations that were used in this study.

Having established an appropriate range of electrolyte concentrations to sufficiently reduce the effects of the electrostatic interactions, a systematic investigation of the sedimentation behavior of silica suspensions with added NaCl and PEO was performed. Polymer concentrations were varied over a wide range and are listed in units of "mg PEO per gram silica", or more simply, "mg/g". Moreover, in subsequent light

absorbance tests, the volume fraction of the silica particles in the suspension was reduced by 1/5 so that the initial absorbance level indicated at least 10% light transmittance. This allowed for stability testing over longer times.

Ordered Addition of PEO and NaCl

Time-dependent absorbance curves for 1.0 μm diameter silica in the presence of PEO1 and 75 mM NaCl are shown in Figure 3.4. Absorbance data for the bare silica suspensions, which begins to fall in a similar "step change" as the suspensions with added PEO after approximately 6 hours, have been included as reference points. At a high concentration of PEO1 (32 mg/g), rapid settling of the suspension occurs. This may be a result of bridging and/or depletion flocculation.

At high adsorbed amounts, long tails extend far away from the particle surface into the solution and contribute significantly to the segment density profile of the adsorbed polymer at relatively large distances [Scheutjens and Fleer (1979, 1980)]. Moreover, since the added amount of PEO1 is considerably higher than what would be required for full coverage, there would be a fair amount of polymer chains free in the solution that may increase the influence of depletion forces.

With just a relatively small amount of PEO1 (1.6 mg/g) added to the silica suspension, the initial plateau time in the absorbance curve is increased by about 50% over that of the suspension with a higher concentration of added PEO1. At the lower concentration, the adsorbed polymer chains are able to effectively protect the particles from the reduction in electrostatic repulsion that occurs when NaCl is added to the system. At 75 mM NaCl, the electrical double layer thickness (κ^{-1}) has been compressed to approximately 1.1 nm.

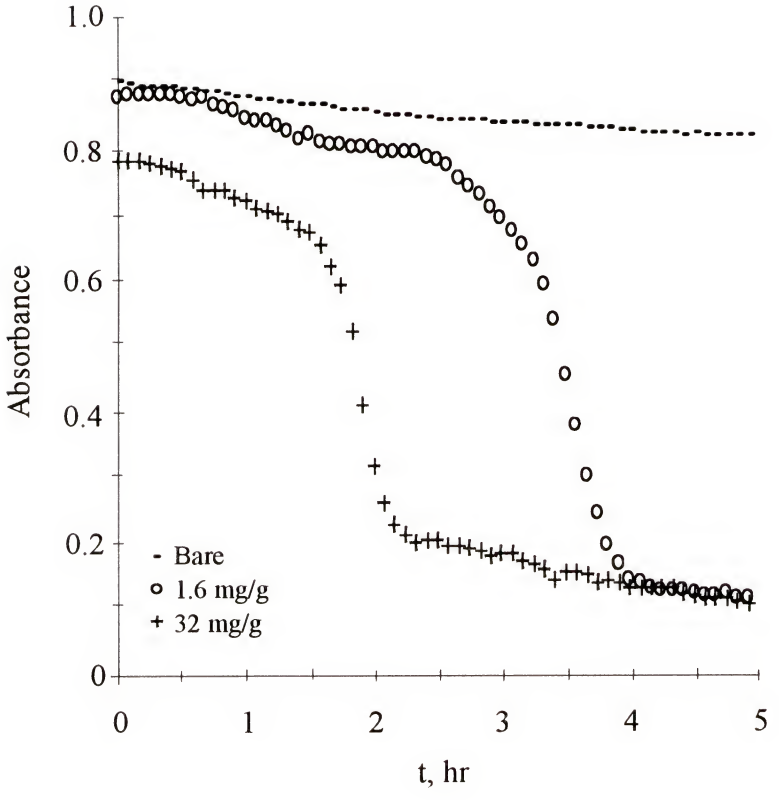

Figure 3.4 Time-dependent settling behavior in the presence of PEO1 via "ordered addition." 1.0 μm diameter silica. $\phi = 0.014\%$. [NaCl] = 75 mM.

Many studies have been conducted to understand the dependence of the adsorbed layer thickness on the polymer molecular weight at full coverages. Theoretical investigations [Scheutjens and Fleer (1979, 1980); Fleer and Scheutjens (1982)] have predicted a square root dependence of the root-mean-square layer thickness on the molar mass for adsorbed linear homopolymers, and experimental results [Kato *et al.* (1981); Killmann *et al.* (1988)] have agreed well with the theory. For PEO adsorbed on precipitated silica, Killmann *et al.* (1985) found

$$\delta = 0.024 MW^{0.49} \tag{3.3}$$

for the dependence of the adsorbed layer thickness (δ) on the molecular weight of the adsorbed macromolecular chains. Using this result, an adsorbed layer thickness of 2.5 nm is obtained for PEO1, using the weight average molecular weight. Therefore, the suspension with 1.6 mg/g added PEO1 can be viewed as effectively sterically stabilized against rapid flocculation when electrostatic repulsion has been reduced.

Size distribution characterizations of the suspensions in Figure 3.4 have been performed, and the results are shown in Figure 3.5. In the presence of NaCl only, a wide range in particle sizes is apparent. This result is expected since the electrostatic interactions have been significantly reduced. However, when the electrolyte is added to the suspension in the presence of adsorbed polymer, the steric layer that is formed is able to prevent significant agglomeration of the particles. This behavior is observed upon a small addition of PEO1. When the polymer concentration is increased, large flocs may be produced through bridging and/or depletion flocculation, and a shift in the average particle size, as shown in Figure 3.5, may occur.

Simultaneous Addition of PEO and NaCl

Figures 3.6 and 3.7 show absorbance vs. time for 1.0 μm diameter silica at various concentrations of PEO1 and PEO2, respectively. Except for the tests that are listed as "Bare" (containing no NaCl or PEO), all electrolyte concentrations are 150 mM. Previous studies under "ordered addition" of PEO1 and NaCl were conducted at an electrolyte concentration of 75 mM. The electrolyte concentration of these suspensions with "simultaneous addition" of PEO and NaCl was increased in order to generate a highly unstable system so that the ability of PEO to restabilize such systems could be

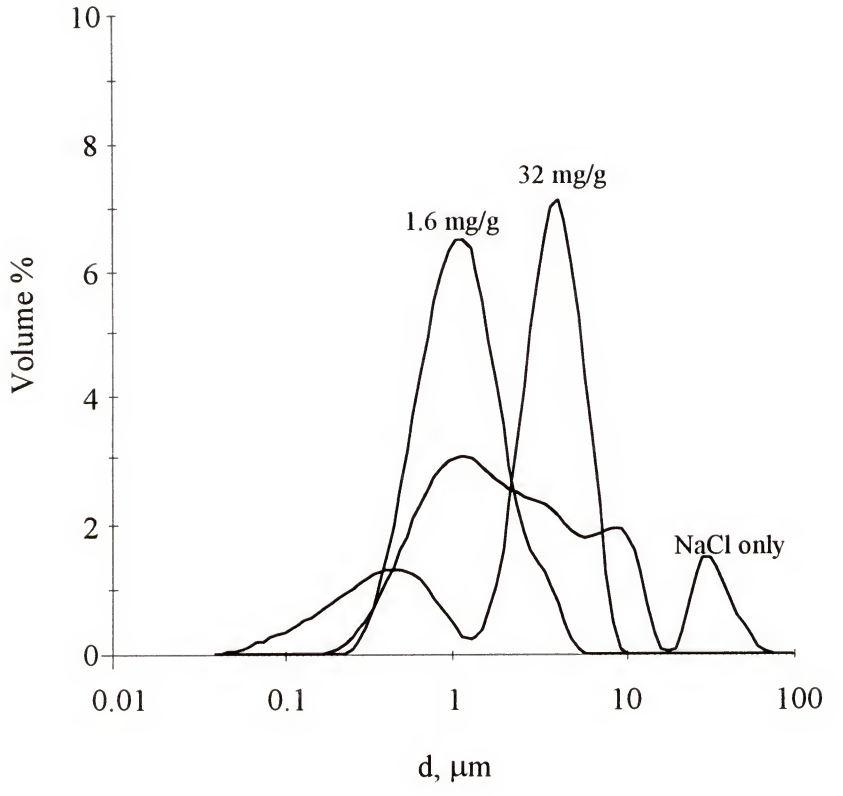

Figure 3.5 Size distribution characterization in the presence of PEO1 via "ordered addition." 1.0 μm diameter silica. $\phi = 0.014\%$. [NaCl] = 75 mM.

studied. At 150 mM, the electrical double layer thickness (κ^{-1}) is approximately 0.8 nm, and rapid settling, as expected, occurs.

Under the range of polymer concentrations considered (0 – 640 mg/g), suspensions with added polyethylene oxide do not settle as quickly as those without added PEO. Similar behavior is observed for PEO1 and PEO2. The most significant decrease in settling behavior (increase in suspension stability) occurs when PEO2 is added to the silica suspensions at a concentration of 64 mg/g. At this polymer concentration, considerable adsorption and a high surface coverage is expected. Moreover, at high coverages, a thick adsorbed layer results because the fraction of

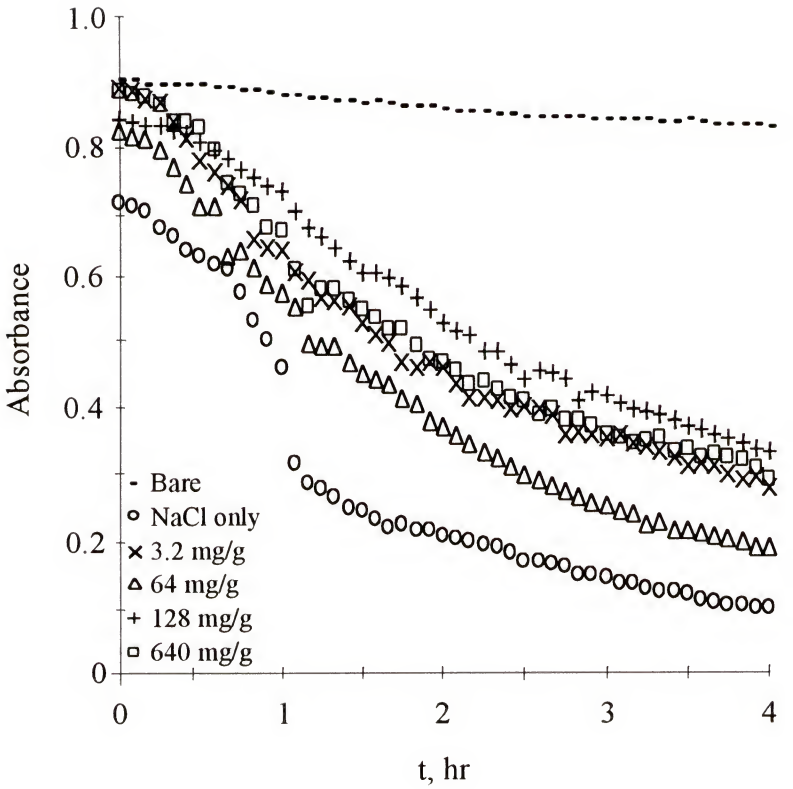

Figure 3.6 Time-dependent settling behavior at various concentrations of PEO1 via "simultaneous addition." 1.0 μm diameter silica. $\phi = 0.014\%$. [NaCl] = 150 mM.

actually adhered or bound polymer segments decreases [Killmann (1976); Scheutjens and Fleer (1979, 1980); de Witt and van de Ven (1992)]. A thick adsorbed layer leads to stronger repulsive forces and a more stable suspension.

Furthermore, PEO2 appears to be more effective than PEO1 in stabilizing the silica suspensions in the presence of 150 mM NaCl although a lower dosage of PEO2 was required. The highest degree of stability with added PEO1 was observed for a polymer concentration of 128 mg/g while 64 mg/g of PEO2 produced an even more stable system that settled less quickly. Adsorbed layer thicknesses have been shown to increase with the molecular weight of the adsorbed polymer chain [Killmann *et al.*

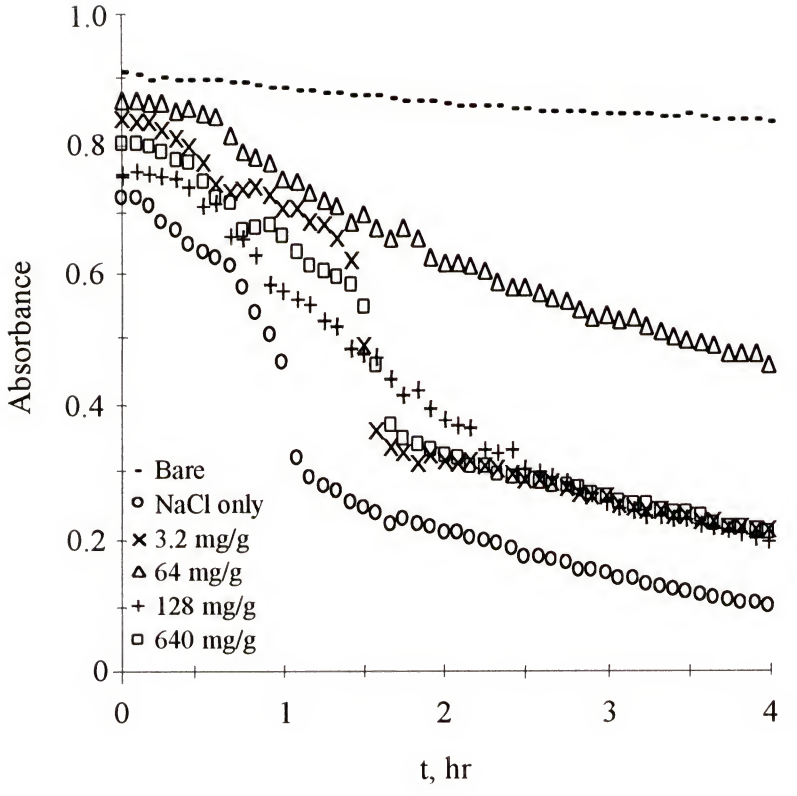

Figure 3.7 Time-dependent settling behavior at various concentrations of PEO2 via "simultaneous addition." 1.0 μm diameter silica. $\phi = 0.014\%$. [NaCl] = 150 mM.

(1985); Chibowski (1990)]. This would also lead to longer-range steric effects for adsorbed layers of PEO2.

The stabilizing effect of PEO2 at 64 mg/g was also verified visually. Portions of suspensions (10 mL) were added to graduated cylinders, stoppered, and allowed to settle undisturbed. The suspension heights were recorded at fixed times. For the suspension containing only NaCl, there was a cloudy region between the clear supernatant and the developing sediment, and the reported suspension height value includes the uppermost portion of this cloudy region. As shown in Figure 3.8, the silica suspension in the presence of PEO2 and NaCl remains suspended over a longer time when compared with

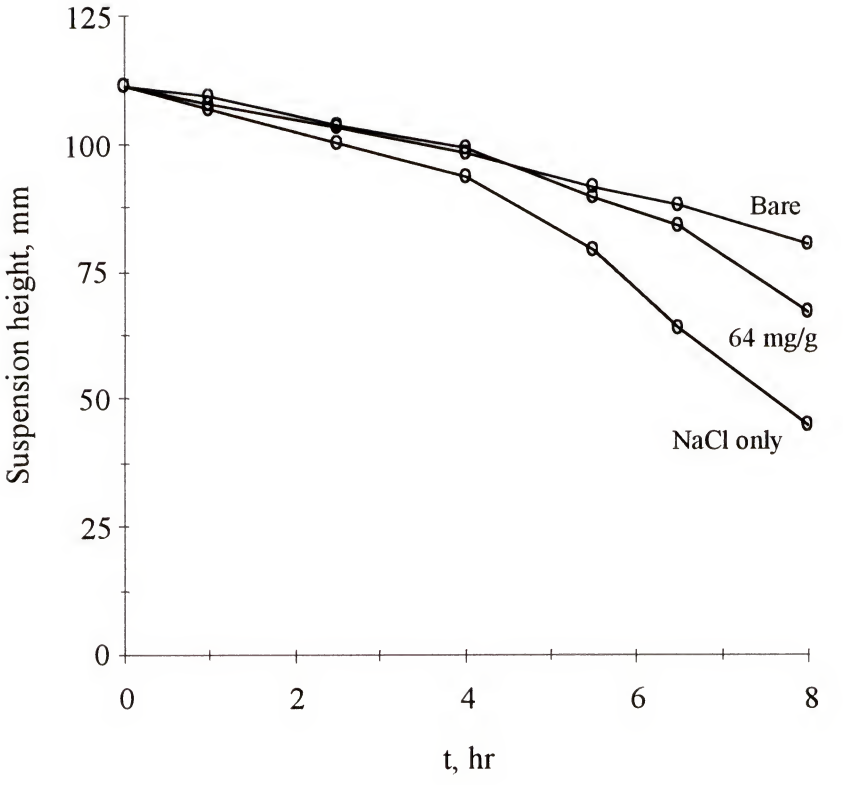

Figure 3.8 Visual settling behavior in the presence of PEO2. 1.0 μm diameter silica. ϕ = 0.014%. [NaCl] = 150 mM.

the polymer free suspension with 150 mM NaCl. (The lines in Figure 3.8 have merely been added to guide the eye.)

Summary

The stability of silica suspensions was manipulated by adding an electrolyte (NaCl) and polyethylene oxide and studied using time-dependent UV-visible spectrophotometry. In stabilizing the suspensions, the polymer concentration and

molecular weight and the sample preparation procedure all seem to play a role in determining whether or not the suspension will be stable.

Upon ordered addition of the polymer and electrolyte, a small amount of PEO is effective in preventing flocculation of the particles. A higher polymer concentration leads to the formation of large flocs, and rapid settling occurs. Under simultaneous addition of PEO (of two different molecular weights) and NaCl, larger concentrations of polymer are required for steric stabilization. Furthermore, the higher molecular weight polymer appears to be more effective in stabilizing the silica suspensions although a lower overall concentration was required. This result is probably due to the formation of a denser adsorbed layer for the higher molecular weight PEO.

CHAPTER 4
THEORETIAL ANALYSIS OF SEDIMENTATION

When a homogeneous mixture of solid particles in a liquid is allowed to stand over time, the particles will eventually settle under the influence of gravitational forces. The rate at which the particles settle will depend on their size, shape, and concentration [Batchelor (1972)]. The dependence of particle size and shape on the sedimentation behavior takes the simplest possible form when the particles are identical rigid spheres of a small size, such as in the colloid range. In this case, the particle Reynolds number is small, and the particle is in the Stokes regime. The dependence on particle concentration arises from the complex interactions between the particles. These interactions are very significant when the particle separation distance decreases.

The sedimentation behavior of very dilute suspensions of rigid, spherical, non-interacting particles can be adequately described by Stokes equation. The settling of more concentrated suspensions, however, is a considerably more involved problem. Since the distance between the particles decreases, complex interactions between the particles occur. As a consequence, particles no longer settle independently of one another, and many-body interactions are no longer insignificant. Moreover, at volume fractions above 0.05, the total density and viscosity of the system increases [Tadros (1980)], further complicating any attempt to understand and/or describe the settling behavior.

Brownian Motion and Particle Diffusion

As discussed in Chapter 1, the total force on a Brownian particle can be split into two parts. The first part is a frictional force resulting from viscous drag, and the second part is a fluctuating force characteristic of the molecular agitation experienced by the particles (Equation 1.1):

$$m\frac{du}{dt} = -m\beta u + A(t). \tag{4.1}$$

In terms of the acceleration experienced by the particles, the Langevin equation may be written as:

$$\frac{du}{dt} = -\beta u + \frac{1}{m}A(t). \tag{4.2}$$

If the time scales that are to be considered are long when compared with the viscous relaxation time (i.e., $\Delta t >> \beta^{-1}$), $\boldsymbol{A(t)}$ can be assumed to vary rapidly when compared with the variations in the particle velocity $\boldsymbol{u}$. Therefore, although the particle positions at t and $t+\Delta t$ are only slightly different, $\boldsymbol{u(t)}$ and $\boldsymbol{u(t+\Delta t)}$ will be completely uncorrelated with one another.

Solutions of Equation 4.2 are needed in order to derive all of the relationships (such as particle positions and/or velocities) necessary to understand the motion of Brownian particles. However, Equation 4.2 is not an ordinary differential equation, and hence, its solution is not simple to obtain. First, an explicit form for $\boldsymbol{A(t)}$ is not known, although, in some cases, a description of what it should be can be derived. Furthermore, the fluctuating nature of $\boldsymbol{A(t)}$ makes Equation 4.2 a "stochastic" differential equation, and

its solution will yield probability distributions describing the velocities and positions of the particles, given appropriate initial conditions.

Assuming, again, that $\Delta t >> \beta^{-1}$, the motion of Brownian particles can be described as a diffusion process in the bulk system. In the free field case, the concentration distribution of the particles can be written as

$$\frac{Dc}{Dt} = D\nabla^2 c, \tag{4.3}$$

where D is the diffusion coefficient as described by the Stokes-Einstein relationship:

$$D = \frac{kT}{6\pi a\mu}. \tag{4.4}$$

When the particles experience an outside field of force, the diffusion equation given by Equation 4.3 can be modified to include the acceleration $\boldsymbol{K(r,t)}$ of the outside force as:

$$\frac{Dc}{Dt} = D\nabla^2 c - \frac{1}{\beta}\nabla\cdot(cK) \tag{4.5}$$

or

$$\frac{\partial c}{\partial t} + v\cdot\nabla c = D\nabla^2 c - \frac{1}{\beta}(\nabla c)\cdot K - \frac{c}{\beta}(\nabla\cdot K), \tag{4.6}$$

where $\boldsymbol{v}$ is the velocity of the fluid, and β is given by (Equation 1.2)

$$\beta = \frac{6\pi a\mu}{m}. \tag{4.7}$$

In flowing suspensions, particle diffusivity due to Brownian motion controls the particle transport rate from the bulk of the solution and, therefore, the particle deposition rate [Yiantsios and Karabelas (1998)]. In stagnant systems, $\boldsymbol{v}$ is zero, and over time, the effects of Brownian motion and particle diffusion would be to tend to make all available positions in the fluid equally probable [Batchelor (1972)].

The Effect of Gravity on Brownian Motion

If the external field of force experienced by the particles is due to gravity, an interesting effect on the particle motion results. The *sedimentation* phenomena, as it is known, has been investigated by many researchers under a variety of conditions [Mason and Weaver (1924); Chandrasekhar (1943); Batchelor (1972); Chung and Hogg (1985); Farley and Morel (1986); Lawler (1986)], and it has been shown that understanding sedimentation kinetics is important for determining the performance of many different treatment processes.

In a gravitational field, $\boldsymbol{K}$ can be written as

$$K_x = 0, \tag{4.8a}$$

$$K_y = 0, \tag{4.8b}$$

$$K_z = -\left(1 - \frac{\rho_o}{\rho}\right) g, \tag{4.8c}$$

where ρ is the particle density, ρ_o is the density of the suspending fluid, and g is the acceleration due to gravity. Implicit in the definition of $\boldsymbol{K}$ in Equation 4.8, the coordinate system has been chosen so that the z axis corresponds to the vertical direction, and ρ_o should be less than ρ (or else sedimentation would not occur). Therefore, in a stationary fluid (i.e. $v = 0$), Equation 4.6 becomes

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \frac{1}{\beta}\frac{\partial c}{\partial z} K_z \tag{4.9}$$

or

$$\frac{\partial c}{\partial t} = D\nabla^2 c + \frac{1}{\beta}\left(1 - \frac{\rho_o}{\rho}\right) g \frac{\partial c}{\partial z}, \tag{4.10}$$

where Equation 4.8c has been substituted in for K_z.

Since the only non-zero component of $\boldsymbol{K}$ is K_z, the distribution of particles in the x and y directions is uniform, and the particle distribution will only vary in the vertical direction. Therefore, the appropriate differential equation to solve is

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} + \frac{1}{\beta}\left(1 - \frac{\rho_o}{\rho}\right)g\frac{\partial c}{\partial z} \tag{4.11}$$

or

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} + U_S\frac{\partial c}{\partial z}, \tag{4.12}$$

where U_S is the sedimentation velocity given by (Equation 2.7):

$$U_S = \frac{1}{\beta}\left(1 - \frac{\rho_o}{\rho}\right)g = \frac{2a^2(\rho - \rho_o)g}{9\mu}. \tag{4.13}$$

The second equality in Equation 4.13 is a result of using Equation 4.7 and

$$m = \frac{4}{3}\pi a^3\rho \tag{4.14}$$

for the mass of the particle.

Equation 4.12 describes the concentration distribution, or number density profile, of particles in the vertical direction as a function of time. Solutions of this relationship have been proposed for liquids of finite, semi-infinite, and infinite depth, and different types of initial conditions have been investigated [Mason and Weaver (1924); Chandrasekhar (1943)].

Pulse Initial Concentration

Chandrasekhar (1943) obtained an analytic solution for Equation 4.12 for the initial condition when all of the particles were initially at a height z_o from the bottom of a semi-infinite fluid domain. In his development, $c(z,t)\Delta z$ was viewed as a probability

function and, consequently, the sum of $c(z,t)\Delta z$ over z at a fixed t should be unity. The initial condition in this case is

$$c \to \delta(z - z_o) \tag{4.15}$$

as t approaches zero, indicating that the probability of finding the particles at position z_o is unity and zero everywhere else.

Furthermore, a no-flux boundary condition is imposed at the bottom of the fluid. Therefore,

$$D\frac{\partial c}{\partial z} + U_S c = 0 \tag{4.16}$$

at $z = 0$ for all $t > 0$. Since Chandrasekhar's solution is for a semi-infinite fluid, it is possible for the particles to initially diffuse vertically upward above z_o for a short time when the particle diffusion dominates gravitational convection.

To obtain the solution to Equation 4.12 under the conditions of Equations 4.15 and 4.16, Chandrasekhar first introduced the following variable transformation:

$$w = c\exp\left[\frac{U_S}{2D}(z - z_o) + \frac{U_S^2}{4D}t\right]. \tag{4.17}$$

Upon implementation of the above transformation, Equation 4.12 becomes:

$$\frac{\partial w}{\partial t} = D\frac{\partial^2 w}{\partial z^2}. \tag{4.18}$$

The initial and boundary conditions are also transformed. They reduce to

$$w \to \delta(z - z_o) \tag{4.19}$$

as t approaches zero, and

$$\frac{\partial w}{\partial z} + \frac{1}{2}U_S w = 0 \tag{4.20}$$

at $z = 0$ for all $t > 0$.

Equation 4.18 is the canonical form of the one-dimensional heat equation. The solution, for the initial and boundary conditions given by Equations 4.19 and 4.20, is given by:

$$w = \frac{1}{2(\pi Dt)^{1/2}}\left\{\exp\left[\frac{-(z-z_o)^2}{4Dt}\right]+\exp\left[\frac{-(z+z_o)^2}{4Dt}\right]\right\}$$

$$+\frac{U_S}{D\pi^{1/2}}\exp\left[\frac{U_S^2 t}{4D}-\frac{U_S}{2D}(z+z_o)\right]\int_{\frac{z+z_o-U_S t}{2(Dt)^{1/2}}}^{\infty}\exp(-x^2)dx\,. \qquad (4.21)$$

Using the transformation relation (Equation 4.17) to return to the original variable c, the concentration distribution in the vertical direction as a function of time, and the required solution to Equation 4.12, is given by:

$$c(z,t;z_o) = \frac{1}{2(\pi Dt)^{1/2}}\left\{\exp\left[\frac{-(z-z_o)^2}{4Dt}\right]+\exp\left[\frac{-(z+z_o)^2}{4Dt}\right]\right\}$$

$$\times\exp\left[-\frac{U_S}{2D}(z-z_o)-\frac{U_S^2}{4D}t\right]+\frac{U_S}{D\pi^{1/2}}\exp\left[-\frac{U_S}{D}z\right]\int_{\frac{z+z_o-U_S t}{2(Dt)^{1/2}}}^{\infty}\exp(-x^2)dx\,. \qquad (4.22)$$

Probability distributions according to Equation 4.22 are shown in Figures 4.1, 4.2, and 4.3 for various particle sizes. The probability of finding a particle at a vertical position between z and $z+\Delta z$ at a time t, given that all of the particles were initially at a horizontal location z_o, is noted by $c(z,t;z_o)\Delta z$. In Figures 4.1, 4.2, and 4.3, particle (silica) diameters of 0.2 μm, 0.5 μm, and 1.0 μm have been used, and z_o was set at 40 mm. Parameters for an aqueous solvent (ρ_o, μ) at 25 °C were also used.

If a large number of particles are all located at the horizontal plane z_o at $t = 0$, particle diffusion will occur due to Brownian motion, and the particles will settle as a result of gravity. As a result, the initial pulse in the concentration profile broadens with

time, resembling a Gaussian distribution. The concentration profile also shifts downward due to particle settling. As particle size decreases, the broadening in the concentration profile is particularly apparent. As more time passes, the distribution broadens further, and the maximum value shifts to lower z values due to the random motions of the particles as they settle. After long times, the probability of finding the particles near the bottom of the container increases. As t approaches infinity, the equilibrium distribution of particles

$$c(z,\infty;z_o)=\frac{U_S}{D}\exp\left[-\frac{U_S}{D}z\right], \tag{4.23}$$

which is known as the Boltzmann distribution and has units of $length^{-1}$, is obtained.

Uniform Initial Concentration

Solution development

The initial condition for the sedimentation experiments described in Chapter 3 is a uniform distribution of particles throughout the sample cuvette. In this section, the development of an analytical expression to describe the concentration profile of a settling suspension of uniformly distributed particles as a function of vertical distance and time is attempted using Chandrasekhar's solution (Equation 4.22) as a starting point. The solution to the problem described in the previous section was obtained by assuming that the particles were all located at a horizontal plane z_o from the bottom of a semi-infinite fluid domain. This initial condition meant that the probability of finding the particles at z_o at $t = 0$ was equal to unity. The initial condition that will now be considered on the concentration profile is that of a uniform initial concentration. So, in this latter case

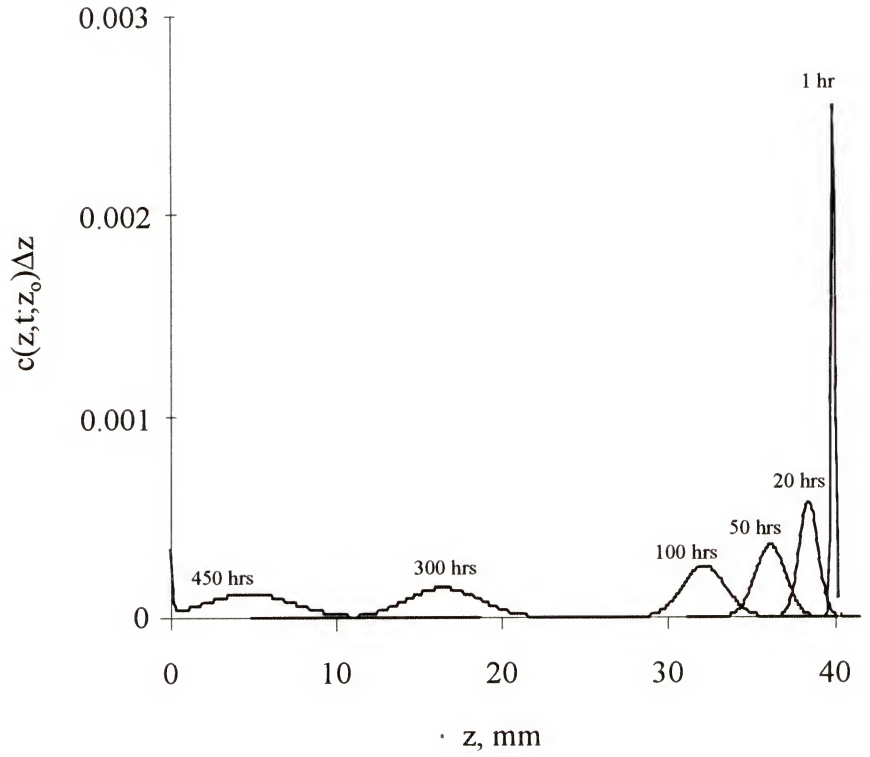

Figure 4.1 Probability distribution of the concentration profile obtained by Chandrasekhar's solution. 0.2 μm diameter silica particles, aqueous medium, 25 °C.

at $t = 0$, it is equally probable to find the particles located at any vertical position z_o between the bottom of the sample cuvette ($z = 0$) and the height h of the suspension in the cuvette.

For the case of a uniform initial concentration at $t = 0$, the particles in the suspension are distributed throughout all available z_o values. So, for this case, the initial condition can be written as

$$c = \phi \tag{4.24}$$

for $0 \leq z \leq h$ and $c = 0$ for $z > h$. In Equation 4.24, ϕ is the particle volume fraction of the suspension. Furthermore, Equation 4.24, a step function, is an integral of the delta

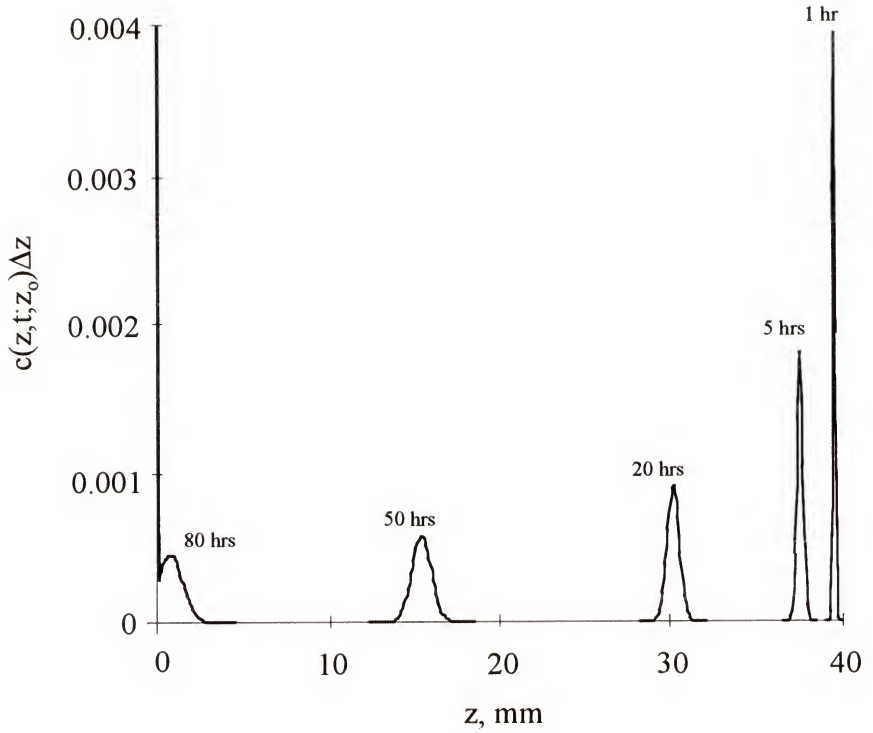

Figure 4.2 Probability distribution of the concentration profile obtained by Chandrasekhar's solution. 0.5 μm diameter silica particles, aqueous medium, 25 °C.

function (Equation 4.15), and the solution to the settling problem with uniform initial concentration can be described by a space-average over Equation 4.22 about z_o for $0 \leq z_o \leq h$, or:

$$c(z,t) = \frac{1}{h}\int_0^h c(z,t;z_o)dz_o \,. \tag{4.25}$$

For a simplified appearance of an algebraically complicated equation, Equation 4.25 is presented in a dimensionless form using the following dimensionless relations:

$$\bar{z} = \frac{z}{D/U_S}, \tag{4.26a}$$

$$\overline{z_o} = \frac{z_o}{D/U_S}, \tag{4.26b}$$

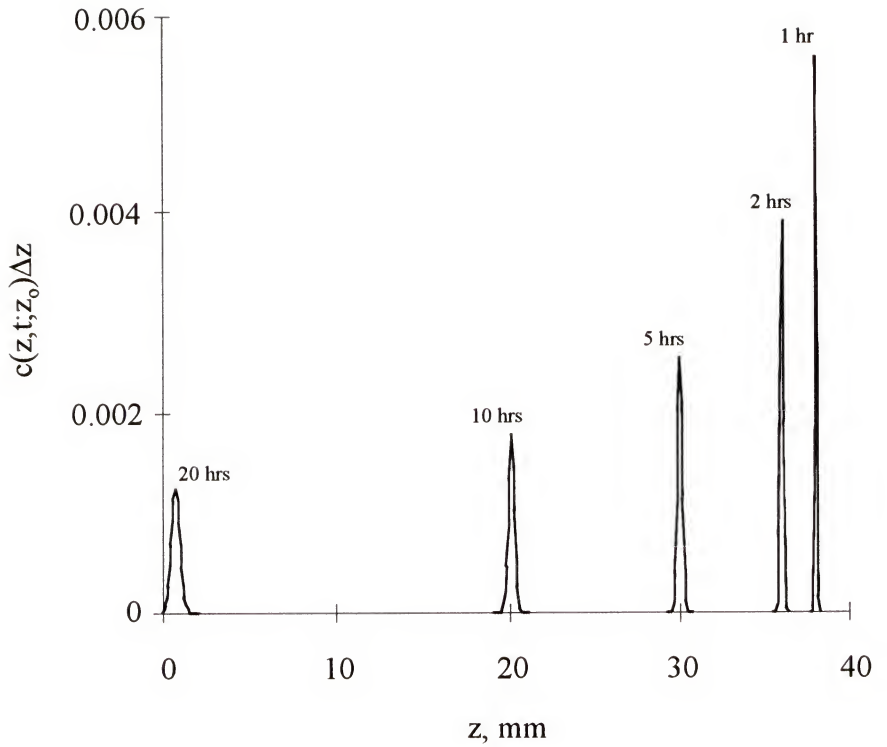

Figure 4.3 Probability distribution of the concentration profile obtained by Chandrasekhar's solution. 1.0 μm diameter silica particles, aqueous medium, 25 °C.

$$\bar{t} = \frac{t}{D/U_S^2}. \tag{4.26c}$$

Here D/U_S is a characteristic length that describes the speed of the particles in the Boltzmann distribution (Equation 4.23). It is approximately 0.8 μm for 1.0 μm diameter particles. The characteristic time scale, D/U_S^2, is about 1.5 seconds for the same size particles. Using Equation 4.26, Equation 4.25 can be expressed in dimensionless form as:

$$c\left(\bar{t},\bar{z}\right) = \frac{1}{2h\pi^{1/2}} \int_o^{Pe} \bar{t}^{-1/2} \left\{ \exp\left[\frac{-\left(\bar{z}-\bar{z}_o+\bar{t}\right)^2}{4\bar{t}} \right] + \exp\left[\frac{-\left(\bar{z}-\bar{z}_o+\bar{t}\right)^2}{4\bar{t}} + \frac{-\bar{z}\,\bar{z}_o}{\bar{t}} \right] \right\} d\bar{z}_o$$

$$+\frac{1}{h\pi^{1/2}}\exp\left(-\bar{z}\right)\int_0^{Pe}\left[\int_{\frac{\bar{z}+\bar{z}_o-\bar{t}}{2\bar{t}^{1/2}}}^{\infty}\exp\left(-x^2\right)dx\right]d\bar{z}_o. \tag{4.27}$$

The upper integration limit in Equation 4.27 is a dimensionless Peclet number, and in this case, it is given by

$$Pe=\frac{hU_s}{D}. \tag{4.28}$$

There are many forms of the Peclet number [Bird *et al.* (1960); Chung and Hogg (1985); Russel *et al.* (1989)], but in essence, it gives the ratio of convective to diffusive forces. Therefore, the relative importance of Brownian diffusion is described by the magnitude of the Peclet number. Low settling velocities and high diffusivities (which occur for smaller particles) result in low Peclet numbers and indicate that the effects of Brownian motion are dominate. However, the value of the Peclet number for which Brownian motion effects become significant varies.

A computer program was written in order to observe changes in the particle concentration c at varied t for a fixed position z as described by the solution given by Equation 4.27. The upper plot in Figure 4.4 corresponds to the time variation of the particle concentration profile at three different positions, and the lower plot is the first derivative of the concentration with respect to time. The results shown are for a 1.0 μm diameter (silica) particle in an aqueous medium at 25 °C, and a value of 40 mm was used for h. The parameters z_o^*, z_1^*, and z_2^* are the fixed z positions, and they differ by 6.35 mm (1/4 inch). Numerically, the z^* values are 30 mm, 23.65 mm, and 17.3 mm,

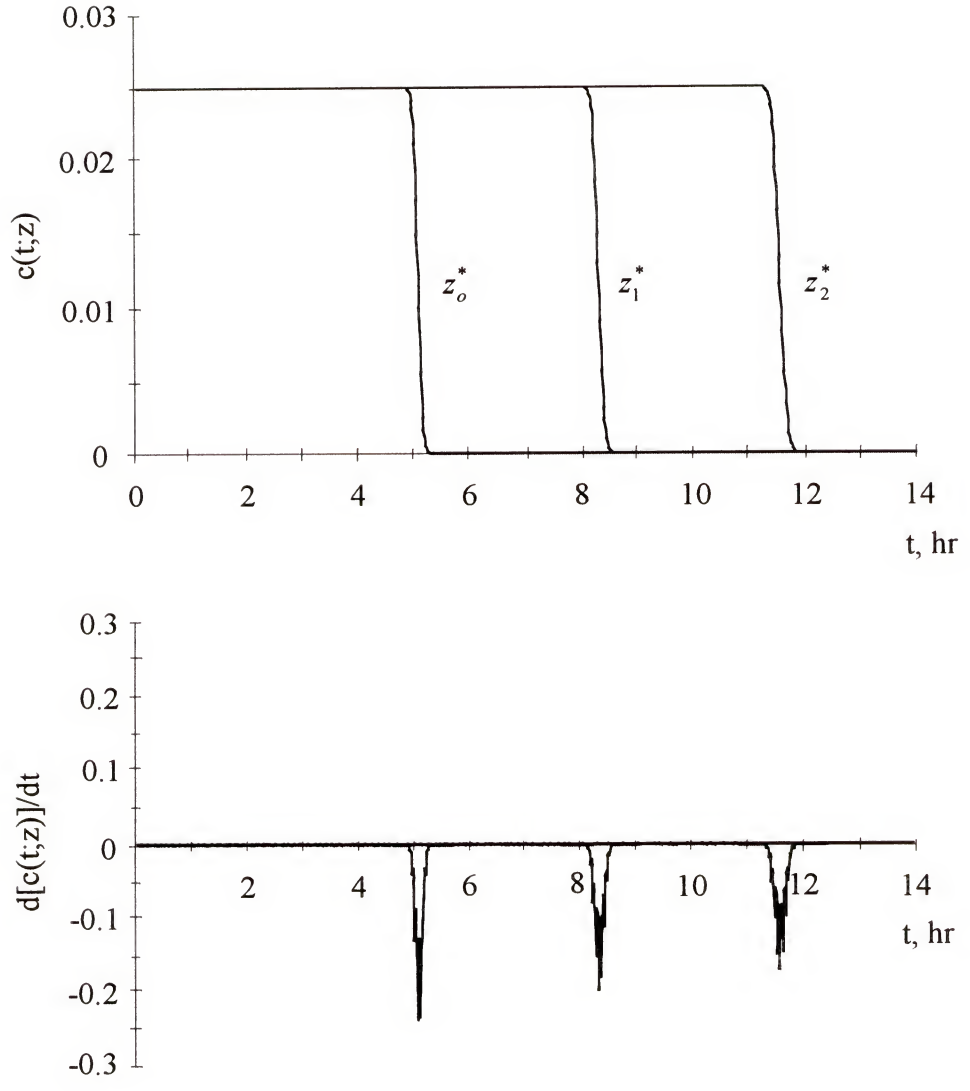

Figure 4.4 Theoretical prediction of a time-dependent concentration profile at fixed z positions. 1.0 μm diameter silica particles, aqueous medium, 25 °C. $z_o^* = 30$ mm, $z_1^* = 23.65$ mm, and $z_2^* = 17.3$ mm.

respectively. (The significance of the choice of these values will be further explained in the next section.)

As illustrated in the first plot in Figure 4.4, there is an initial plateau in all of the concentration profiles. These initial plateaus occur because, at a fixed vertical position (a particular z^* value), no change in the particle concentration is observed. Although the particles are settling, as one particle passes out of the horizontal plane under consideration, another particle drifts into that horizontal plane from above, as long as the particles in the upper region are not depleted. After a particular time (which varies with z^*), there is a sharp decrease in the particle concentration as depletion of the particles in the upper region occurs due to settling of the particles, and the time for this sharp change to occur increases with decreasing z^* value. (Note that h and all z values are measured from the bottom of the fluid.) The three curves in the first plot of Figure 4.4 may also be viewed as the time-dependent downward movement of the particle-depletion zone.

The time derivatives of the concentration profiles are also included in Figure 4.4 (the lower plot). The peaks in the first derivative curves correspond to the inflection points in the upper curves, and the widths of the lower plots give some information with regard to the particle size. Although it is not as obvious in the plots of $c(z,t)$ vs. t, the first derivatives reveal that at lower z^* values, the widths of the $d[c(z,t)]/dt$ vs. t curves increase. This occurs because of particle diffusion resulting from Brownian motion. The increase in the mean displacement of the particles with time is illustrated by the broadening of the time-dependent derivative curves in the lower plot of Figure 4.4. This behavior is equivalent to the broadening of the particle concentration profiles over time as depicted in Figures 4.1, 4.2 and 4.3.

The sedimentation velocity can be determined from time-dependent concentration profiles obtained at different fixed vertical positions by

$$U_S = \frac{\Delta z^*}{\Delta t}, \tag{4.29}$$

where Δz^* is the difference between two fixed vertical positions, and Δt is the time difference between the inflection points in their respective $c(z,t)$ vs. t curves (or the time difference between the peaks in their $d[c(z,t)]/dt$ vs. t curves). By making use of the definition of U_S given by Equation 4.13, the particle size can be calculated by using

$$U_S = \frac{\Delta z^*}{\Delta t} = \frac{2a^2(\rho - \rho_o)g}{9\mu} \tag{4.30}$$

or

$$2a = 2\sqrt{\frac{9\eta}{2g(\rho - \rho_o)} \cdot \frac{\Delta z^*}{\Delta t}}. \tag{4.31}$$

Since the solution given by Equation 4.27 is for a dilute suspension of non-interacting particles, the particle size calculated by Equation 4.31 yields the exact value of 1.0 μm diameter that was used to generate the curves in Figure 4.4.

Comparison with experimental observations

The sedimentation behavior observed by use of the UV-visible spectrophotometer described in Chapter 3 is revisited here to compare with the theoretical analysis given above. Dilute ($\phi = 0.014\%$) suspensions of 1.0 μm (nominal) diameter silica particles in water were allowed to settle over time, and the absorbance at 500 nm was monitored. Approximately 5 mL of the suspensions were added to the sample cuvette (see Figure 3.1), and this corresponded to a suspension height (h) of 40 mm. The level of the liquid height in the cuvette was keep constant with every run.

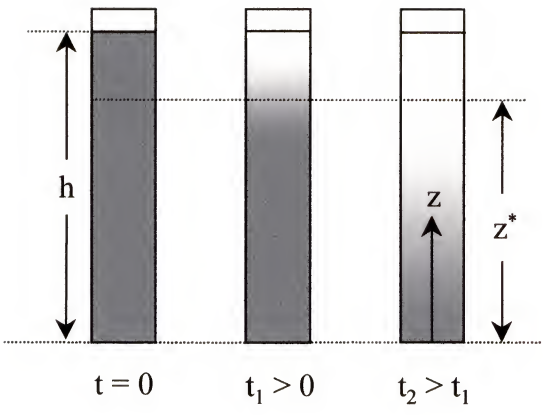

Figure 4.5 Illustration of time-dependent settling behavior and the location of the suspension height (h) and approximate beam position (z^*).

The fixed vertical position from the bottom of the cuvette (z^*) under consideration in the experimental tests is the location of the UV-visible light beam. Although the exact position at which the beam strikes the sample cuvette is unknown, the difference in fixed vertical positions between successive time-dependent absorbance tests was maintained constant at1/4 inch. Square elevation stages of 1/4 inch in thickness were attached to the base of the sample cuvettes in order to vary the beam location by a predetermined amount. An illustration of the time-dependent settling behavior of the suspensions, the location of the suspension height, and the approximate beam location (in the absence of any elevation stages) is shown in Figure 4.5. The position of the UV-visible light beam passing through the suspension in the sample cuvette is fixed in space, and the variation of the local particle concentration (which is proportional to the light absorbance) with time at z^* is measured by the spectrophotometer.

The experimental results for the dilute suspensions of 1.0 μm (nominal) diameter silica are shown in Figure 4.6. The absorbance curve to the far left was obtained without

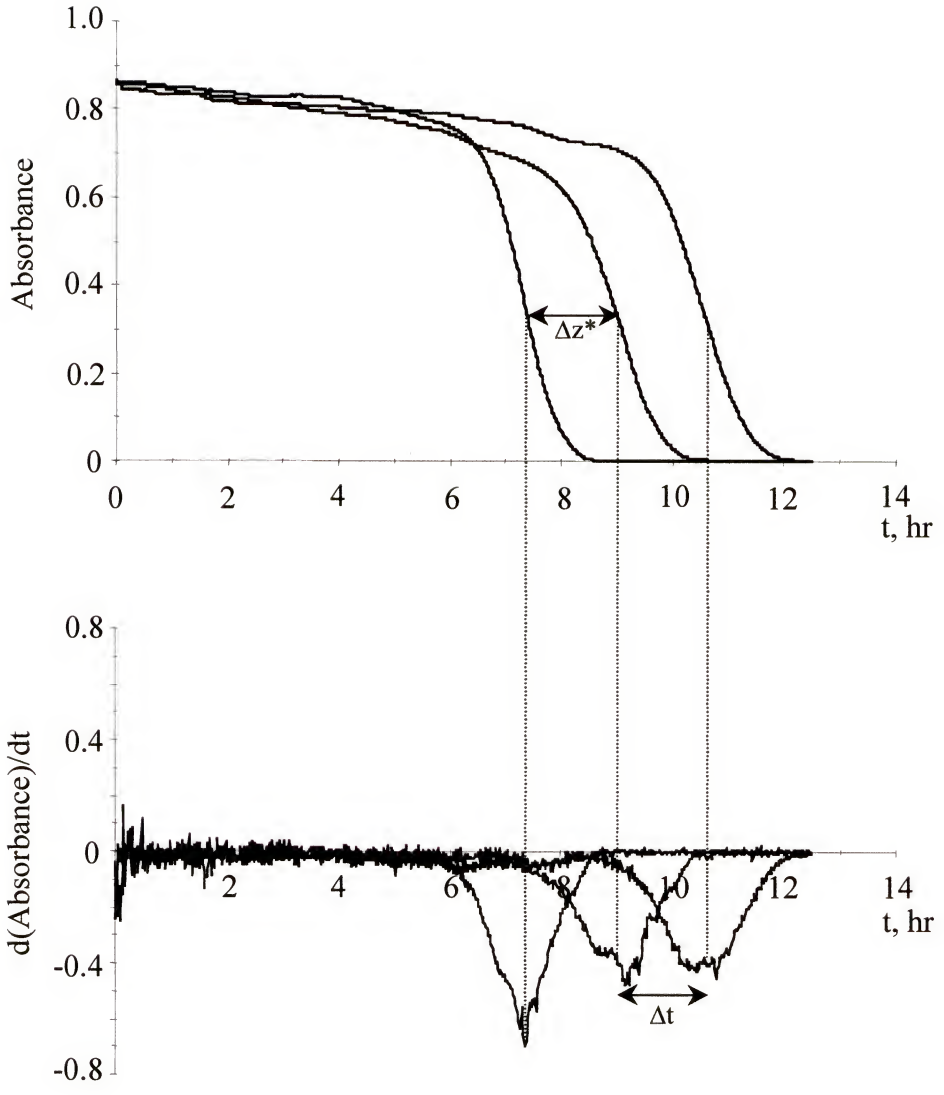

Figure 4.6 Experimental time-dependent concentration profile at fixed z positions. 1.0 μm diameter silica particles, aqueous medium, 25 °C. $\Delta z^* = 6.35$ mm.

an elevation stages. The second and third curves were generated using one and two elevation stages, respectively. As in Figure 4.4, the upper plot in Figure 4.6 corresponds to the particle concentration profile (absorbance vs. t), and the lower plot is the first derivative of the concentration with respect to time (d[absorbance]/dt vs. t). The initial plateau regions in Figure 4.6 are fairly horizontal. The deviations and fluctuations observed at the initial (lower) times result because the silica powder is not completely monodisperse. The slight polydispersity of the silica powder also accounts for the gradual decrease in the light absorbance as the particles settle past the UV-visible light beam position. Again, the inflection points in the absorbance curves correspond to the peaks in the curves of the first derivatives, and the widths of the d[absorbance]/dt vs. t plots are indicative of the increase in the mean particle displacement with time that occurs as a result of the combined effects of Brownian motion and gravitational settling.

As in the theoretical development, the value of Δz^* (the stage thickness) is 6.35 mm (1/4 inch). From Figure 4.6, an average Δt value of approximately 1.48 hours was obtained. From these data, a particle diameter of 1.48 μm was calculated using Equation 4.31. An average (peak) value of 1.15 μm was obtained for the diameter of the 1.0 μm (nominal) diameter silica powder via a Coulter® Particle Size Analyzer (see **Materials** section in Chapter 3). The theoretical predictions compare rather well with the experimental results. Although the silica powder used for the experimental tests in Figure 4.6 has a narrow size distribution, the particles are not exactly monodisperse. The particle size distribution may contribute to the difference in particle sizes obtained by theoretical and experimental methods.

Summary

For dilute colloidal suspensions, theoretical predictions of the sedimentation behavior are possible. The concentration profile of the settling particles can be described as a function of time and vertical distance under a variety of boundary and initial conditions. In this study, an analytical solution in the form of an integral was presented as a method to determine time-dependent concentration changes of a settling suspension at a fixed vertical position. By studying the particle concentration as a function of time at different fixed vertical positions, the average particle size could be determined. Experimental tests were conducted using the UV-visible spectrophotometer, and the results compared reasonable well with the theoretical predictions. Therefore, UV-visible spectrophotometry may serve as a method to characterize the average particle size of a colloidal suspension.

CHAPTER 5
SHEAR VISCOSITY BEHAVIOR

The rheological properties of colloidal suspensions are of interest to many systems and processes. Some of these include cosmetic and drug preparations, food processing, road resurfacing, sewage disposal and water treatment, just to name a few. Real systems and processes, including those previously listed, are polydisperse. However, simplified monodisperse and bidisperse suspensions are often used as models to further understand the flow behavior of polydisperse systems.

The complex rheological behaviors of colloidal suspensions are affected by the hydrodynamic interactions between the particles and non-hydrodynamic colloidal forces (as described in Chapter 1). These forces, in conjunction with particle size, shape, and size distribution, lead to microstructures [van der Werff and de Kruif (1990); Wagner and Klein (1991); Graham *et al.* (1992)], non-Newtonian flow characteristics [Barnes (1989), Kawaguchi *et al.* (1991); Boersma *et al.* (1992)], and various phase behaviors and instabilities [Hoffman (1972)]. Therefore, the rheological properties of these systems are often studied in order to understand their behavior in relation to physical stability, possible processing conditions, and increased levels of solids loading.

This study focuses on concentrated monodisperse suspensions and bidisperse suspensions in which two different size particles are mixed in different proportions. The shear rate dependent shear viscosities of the monodisperse and bidisperse suspensions are measured using a standard rheological procedure that incorporates time-dependent shear

intervals. The standard procedure was developed in order to understand time effects on the shear viscosity and to ensure that the data reported were accurate representations of the rheological behavior of the systems under study. The results of the shear viscosity measurements are compared with published observations, and interpretations of the results in terms of the polydispersity and structural development of the suspensions are given.

Materials and Methods

Monodisperse suspensions were prepared by addition of silica powders (0.5 μm, 1.0 μm, 1.5 μm diameter) to distilled deionized water to produce an initial total volume fraction of 0.25-0.35. These intermediate preparations were ultrasonicated for approximately three hours; then, additional silica was added to increase the total volume fraction of the monodisperse suspensions to the desired final value. The final preparations were ultrasonicated for an additional three hours. Bidisperse suspensions were prepared by mixing, in different proportions, two monodisperse suspensions of the same total volume fraction. In all cases, a portion of the smaller particle monodisperse suspension was added to the suspension of larger particles.

The shear viscosities of these suspensions were measured using a cone-and-plate viscometer with a 1° cone angle and a 37.5 mm cone radius (see Figure 5.1). The gap height between the cone and the plate was 50 μm—more that 30 times the diameter of the largest particle size. During the tests, the viscometer plate was maintained at a constant temperature of 25 °C, the shear rate was controlled via a computer interface, and a

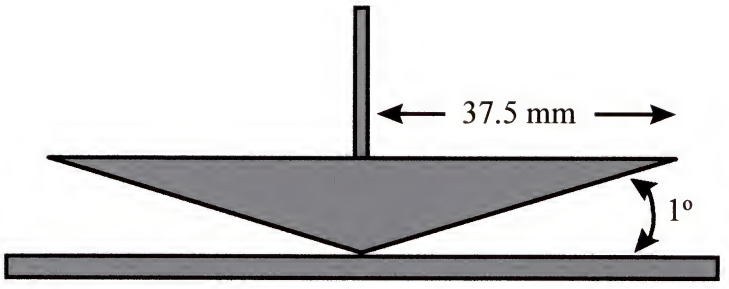

Figure 5.1 Schematic of cone-and-plate viscometer geometry.

humidity pad was used to minimize any potential evaporation of the solvent during the experiments. For each test, the shear viscosity, torque, and shear stress were measured simultaneously.

Concentrated suspensions often show non-Newtonian flow behaviors. Moreover, in measuring the shear viscosities of colloidal suspensions, in addition to shear rate dependencies, time-dependent effects are frequently observed [Huang (1998); Lemke *et al.* (1999)]. Besides time-dependent thixotropic (decreasing viscosity at a constant shear rate) and rheopectic (increasing viscosity at constant shear) behaviors, large fluctuations in the instantaneous shear viscosity may occur. These fluctuations often depend on the state of the material, the flow conditions, and the experimental technique being used. Therefore, a standard rheological procedure is needed to ensure that the reported shear viscosity is an accurate representation of the system being measured and that reproducible data can be obtained.

As a first step in developing a standard rheological procedure, time-dependent measurements of the shear viscosities of a few test systems were measured at various shear rates. Figure 5.2 contains data for one test system of 1.0 μm diameter silica particles at a volume fraction of 0.50, and the results are consistent with other

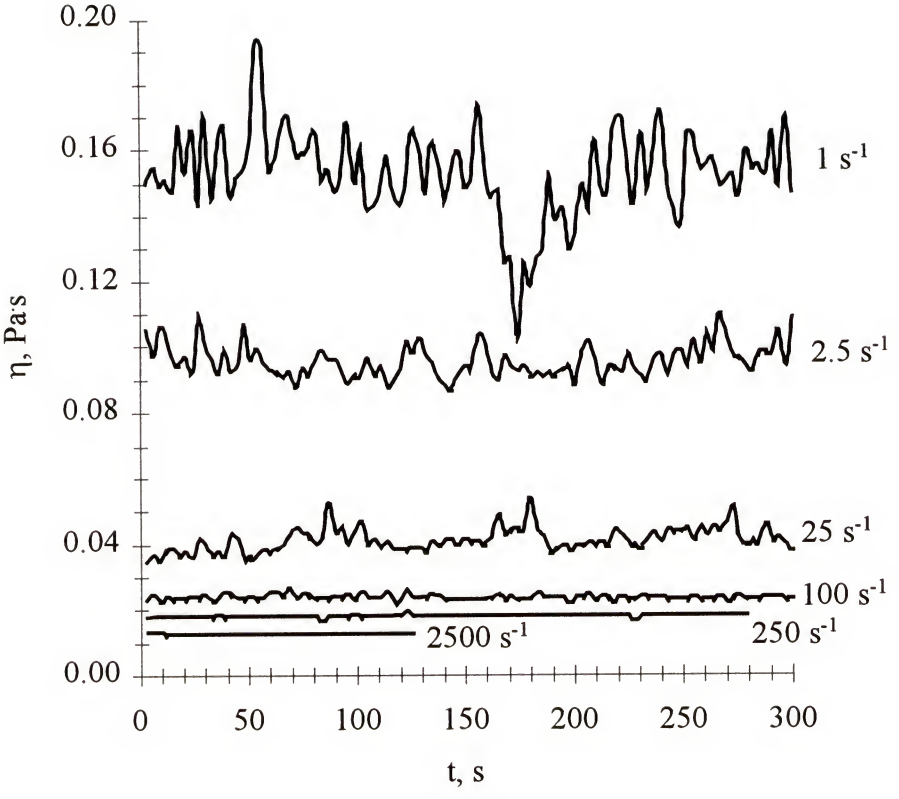

Figure 5.2 Time-dependent shear viscosity at various shear rates. 1.0 μm diameter silica. $\phi = 0.50$.

measurements. Over long times, the viscosity fluctuated around an average value, and the fluctuations increased as the shear rate decreased. At low shear rates ($< \sim 1\ s^{-1}$), these fluctuations could result in considerable errors if only instantaneous values of the shear viscosity were taken into account when reporting the data. Therefore, these time-dependent effects were incorporated into the development of a standard rheological procedure that would screen out the fluctuations when measuring the shear viscosity.

The standard measuring procedure that was developed consisted of a shear rate interval sweep from 5000 s^{-1} down to 0.0025 s^{-1} and then back up to 5000 s^{-1}. The one-minute shear rate intervals were each followed by a one-minute "rest" period during

which time no shear was imposed. Also, a two-minute preconditioning period at 100 s^{-1}, followed by a two-minute "rest" period, was included before the beginning of the shear rate interval sweep.

In studies to investigate possible thixotropic systems, a hysterisis loop is often used [Huang (1998)]. In a hysterisis loop, the shear stress is monitored as the shear rate is increased from zero to a maximum value and then decreased from that maximum value back to zero. The procedure developed in this work is a reverse hysterisis loop. In addition to yielding information regarding instantaneous viscosity fluctuations, possible thixotropy may also be detected by using this reverse loop due to the incorporation of the "rest" periods (although there were no indication of thixotropy in the preliminary tests).

During each interval, i.e. at each (constant) shear rate, three viscosity, torque, and shear stress measurements were recorded. The values were compared within the interval and with the values in the corresponding upward or downward interval, and the values were excepted if they fell within 2% of one another if no thixotropy was detected. The final value reported for the shear viscosity was the average of (at least) three to (at most) six recorded data. The total testing time for the shear rate interval sweep program, including rest periods, was 52 minutes. Although this testing procedure was rather long, no evidence of solvent evaporation was observed when the tests were concluded.

Monodisperse Suspensions

Before proceeding to bidisperse systems, the shear viscosities of monodisperse suspensions were measured at varied shear rates using the above mentioned shear rate

interval sweep program. Figure 5.3 shows shear viscosity as a function of shear rate for the three different particle sizes at a total volume fraction of 0.59. This plot shows that the viscosity decreases as the particle size increases. The characteristic shear-thinning behavior resulting from three-body and higher interactions and structure breaking as the material is sheared is also apparent in the curves for the three different size particles [Russel *et al.* (1989); Boek *et al.* (1996)]. Moreover, shear-thickening can be seen at the higher shear rates where interparticle forces are dominated by shear forces [Bossis and Brady (1989); Boersma *et al.* (1990, 1992); Bender and Wagner (1996)]. Although the shear-thickening observed here is not very strong, the behavior shown in Figure 5.3 is reproducible.

The effect of particle size on the shear viscosity can be described in terms of the electrostatic nature of the suspensions. The interparticle interactions resulting from these forces become the most significant as particle size decreases. As shown in Equation 1.7, the electrical double layer thickness is not a function of the particle size; therefore, the double layer thickness is equivalent for different size particles of the same chemical nature. Thus, under a certain physicochemical condition, suspensions of larger particles are less repulsive than suspensions of smaller particles because the *relative* thickness of the electrical double layer is smaller for larger particles. This effective shorter-range of electrostatic interactions leads to a lower shear viscosity for large particle suspensions.

Suspensions of hard spheres, i.e. those without interparticle interactions, are affected by viscous and thermal forces and the total volume fraction. Therefore, the viscosity of hard sphere suspensions should depend only on the volume fraction and the Peclet number [Woods and Krieger (1970); Russel *et al.* (1989); van der Werff and de Kruif

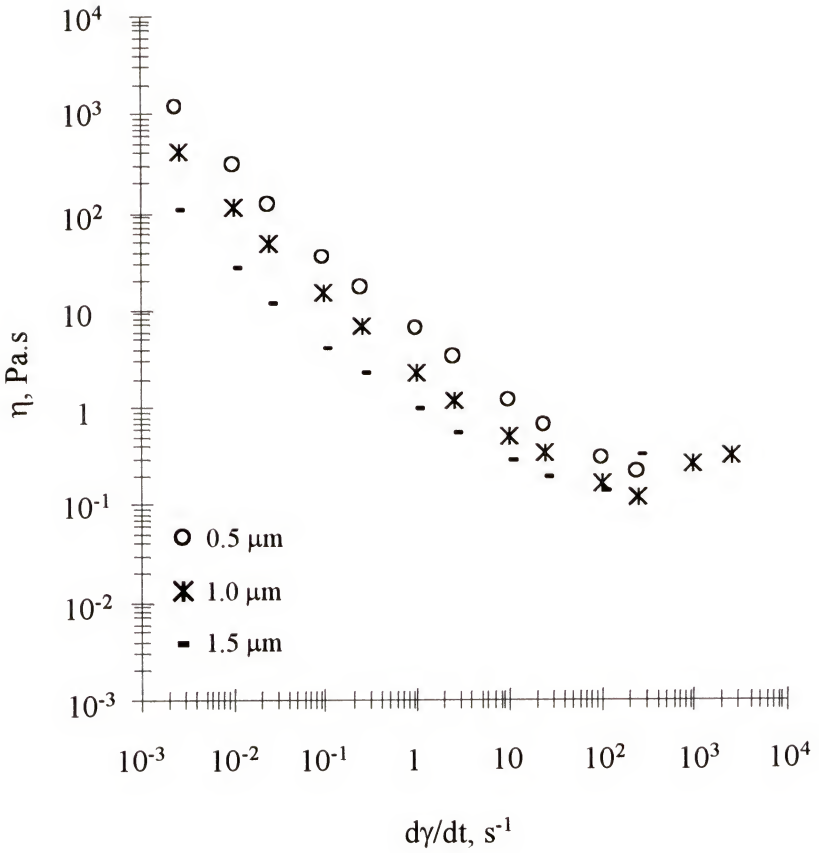

Figure 5.3 Shear viscosity as a function of shear rate for various particle sizes. $\phi = 0.59$.

(1990)]. The Peclet number, a dimensionless shear rate which may give the ratio of viscous to thermal forces, can be expressed as [Russel *et al.* (1989)]:

$$Pe = \frac{\mu a^3}{kT}\left(\frac{d\gamma}{dt}\right), \tag{5.1}$$

where μ is the viscosity of the fluid medium, a is the particle radius, k is Boltzmann's constant, T is the absolute temperature, and $d\gamma/dt$ is the shear rate. Thus, at a fixed volume fraction, a plot of the relative shear viscosities (η/μ) of suspensions of various particle sizes as a function of the Peclet number should superimpose for hard spheres.

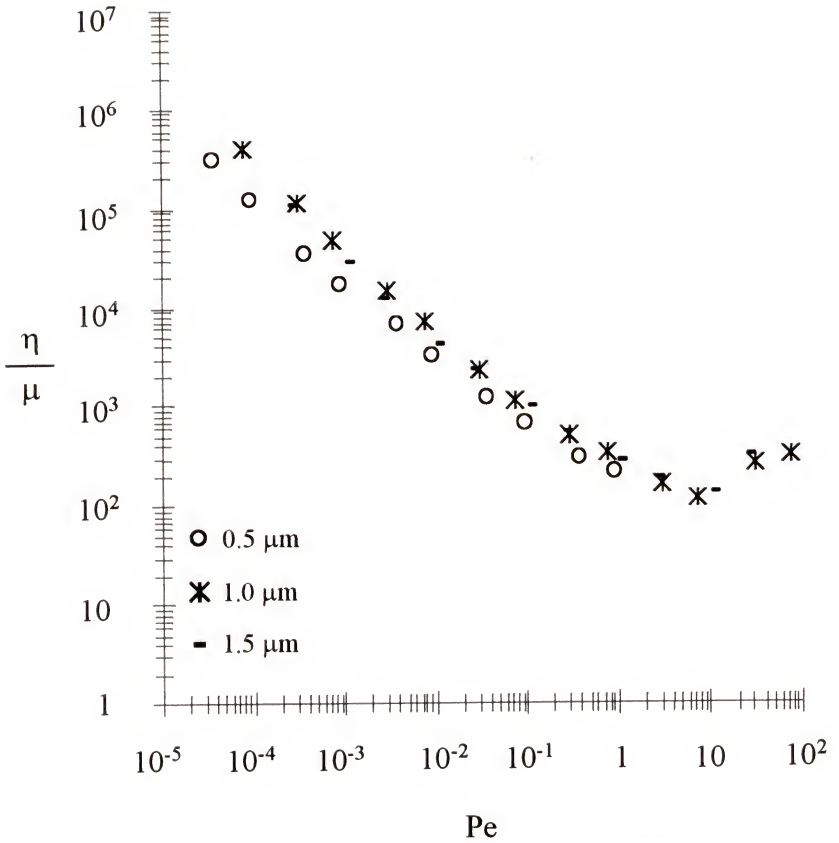

Figure 5.4 Relative shear viscosity as a function of Peclet number for various particle sizes. $\phi = 0.59$.

Figure 5.4 is a dimensionless plot of the results shown in Figure 5.3. In this plot, the shear viscosity of the suspension (η) has been normalized by the viscosity of the fluid medium (μ) to obtain the relative viscosity, and the shear rate has been transformed into a Peclet number as described by Equation 5.1. Since silica particles are charged in aqueous media, some deviation from the hard sphere case can be seen at low Peclet numbers where the interactions resulting from interparticle forces are dominant. At high Peclet numbers, hydrodynamic forces dominate interparticle forces, and considerable agreement with hard sphere theory can be observed. A closer look at Figure 5.4 also shows that there is more of an overlap in the data when comparing the 1.0 μm and the 1.5 μm

diameter particle suspensions. These two particle sizes have the smallest particle size ratio, and hence, the relative thicknesses of their electrical double layers are more closely related.

Bidisperse Suspensions

For bidisperse suspensions, in addition to the total volume fraction of the particles, parameters of interest include the particle size ratio (α) and the relative volume fraction (β)—which is usually defined as the ratio of the volume of the small particles to the volume of both the small and large particles. The shear viscosity of bidisperse suspensions of 0.5 μm and 1.0 μm diameter particles, in which the total volume fraction was maintained constant while varying the relative volume fraction, was measured. Figure 5.5 shows shear viscosity as a function of relative volume fraction at a total volume fraction of 0.50 for three different shear rates. (The lines have been added to guide the eye.) The endpoints are results obtained for the two monodisperse suspensions. A minimum in the suspension viscosity was observed at β values of approximately 0.2. This minimum behavior has also been observed in zero and infinite shear viscosities [Rodriguez *et al.* (1992)], in dynamic viscosity measurements [Kim and Luckham (1993); Gondret and Petit (1997)], at increased pH and with the addition of an electrolyte [Zaman *et al.* (1996); Wilson *et al.* (1997)], and in suspensions of non-colloidal particles [Chang and Powell (1994)].

The minimum in the suspension viscosity at a certain relative volume fraction is due to more efficient packing in relatively polydisperse systems. Furthermore, as the

particle size ratio increases, the minimum in the viscosity of a bidisperse suspension is expected to deepen [Wagner and Woutersen (1994)]. This result is expected because, at very large particle size ratios, the smaller particles would be able to more efficiently fill the void spaces in between the larger particles. In essence, the smaller particles would appear to behave as part of the suspending medium, and the suspension may be viewed as a monodisperse system with regard to the larger particles [Mooney (1951); Chong *et al.* (1971); Storms *et al.* (1990)]. The highest maximum packing fraction would also be expected in this case.

For a given value of β, the relative shear viscosity ($\eta_r = \eta/\mu$) and the total volume fraction (ϕ) were used to determine the maximum packing volume fraction (ϕ_m) for the results shown in Figure 5.5 using the Maron-Pierce relation (Equation 2.3):

$$\eta_r = \left[1 - \frac{\phi}{\phi_m}\right]^{-2} . \tag{5.2}$$

In Figure 5.6, the maximum packing volume fraction goes through a maximum at β values of approximately 0.2, which corresponds to the minima observed in Figure 5.5.

The effect of particle polydispersity on the change in the compressibility factor was studied by Dickinson (1978). He found that the van der Waals approximation predicted that the pressure of a polydisperse system was always lower than that of a monodisperse system with the same total volume fraction. Moreover, in studying the viscosity behavior of bidisperse suspensions of internally-cross-linked polystyrene lattices in an organic solvent (bromoform), Rodriguez *et al.* (1992) found that the minimum in the zero and infinite shear viscosities at a particular value of β corresponded

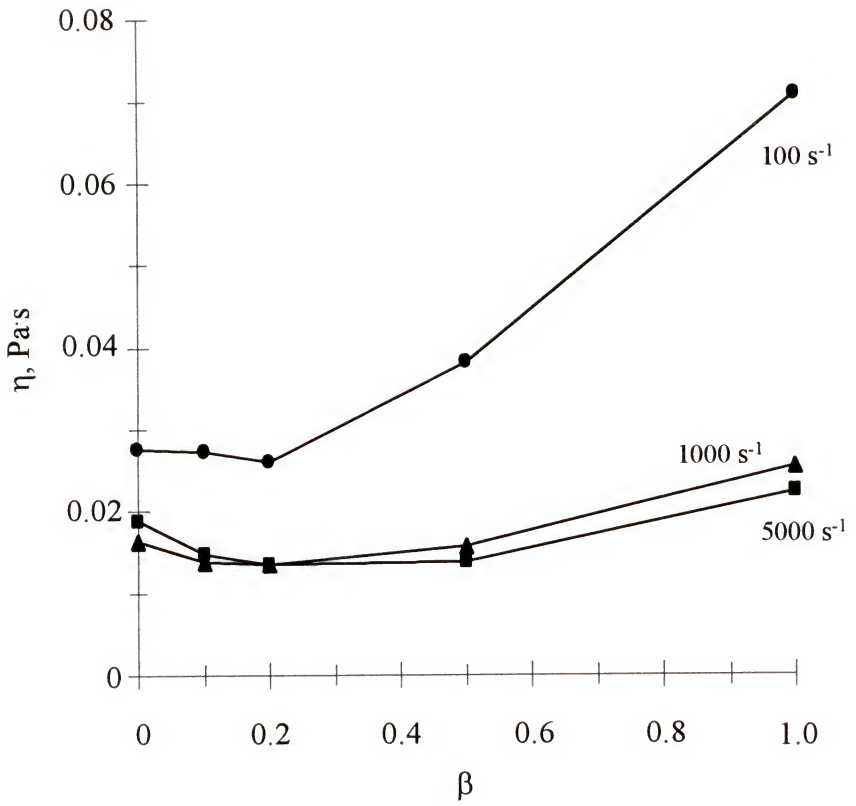

Figure 5.5 Shear viscosity as a function of relative volume fraction at various shear rates for bidisperse mixtures of 0.5 μm and 1.0 μm diameter silica. $\phi = 0.50$.

to a minimum in the osmotic compressibility for a binary mixture of hard spheres [Mansoori *et al.* (1971)]. Similar results were also obtained by Kim and Luckham (1993) for the elastic modulus, dynamic viscosity, and osmotic pressure of mixtures of polystyrene latex particles with a particle size ratio of approximately 6.9. These results indicate that viscosity and compressibility are related, and it was proposed that the former could be calculated from the latter [Rodriguez *et al.* (1992)].

Jacobson (1998) studied the equilibrium and dynamic structure development under shear of bidisperse colloidal systems and monitored the osmotic compressibility as

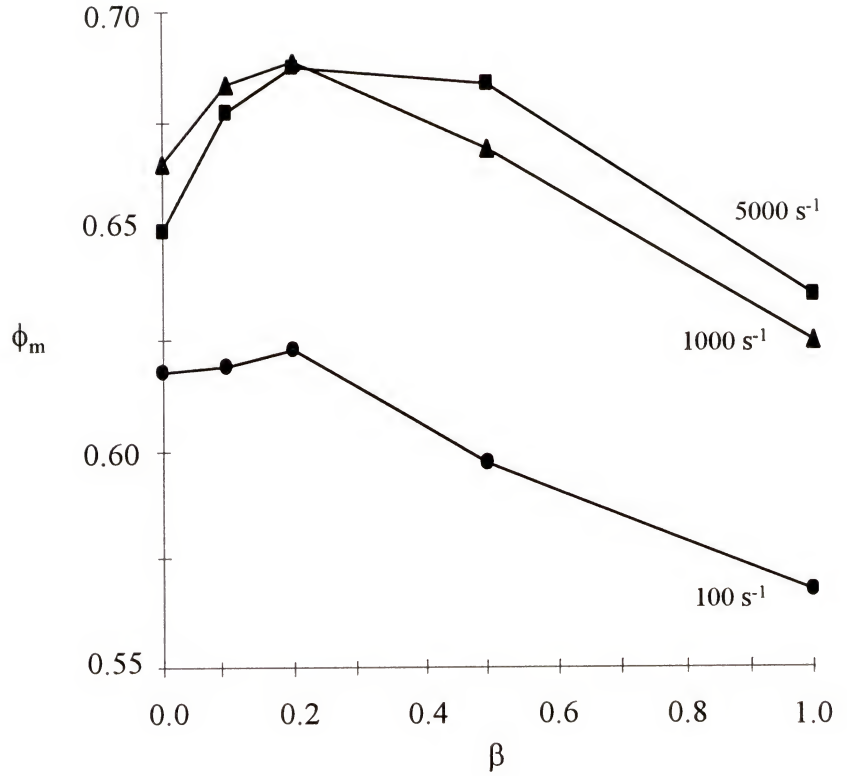

Figure 5.6 Maximum packing volume fraction (ϕ_m) as a function of relative volume fraction (β) at various shear rates for bidisperse mixtures of 0.5μm and 1.0 μm diameter silica. $\phi = 0.50$. (ϕ_m calculated using the Maron-Pierce relation.)

a function of relative volume fraction. His results showed that upon introduction of small particles (a slight increase in β) while maintaining the same overall volume fraction, the hexagonal packing structure of the large particles transformed into a cubic structure at the same location in which β reached a minimum. Therefore, it would appear that the higher packing of particles, which corresponds to a minimum in the viscosity and osmotic compressibility at a given relative volume fraction, is a consequence of the structural changes that occur in the suspensions.

Summary

Understanding the rheological properties of colloidal suspensions is essential to many processes and phenomena. How the material behaves under shear can play a major role in transport, handling, and processing. It has been observed that reductions in suspension viscosity can be achieved by increasing the polydispersity of the suspension. One advantage of this result is that it is possible to achieve higher levels of solids loading while at the same time maintaining overall processability. In addition, this minimum in the shear viscosity of a bidisperse suspension at a particular β value is apparently linked to microstructural changes that occur in the suspension during equilibrium and dynamic conditions.

Moreover, the manner in which rheological properties are measured should be considered. Due to time-dependent behaviors that may result, care must be taken so that an appropriate technique that addresses specific issues that may arises in acquiring accurate and reproducible data is developed. The standard measuring procedure developed in this work to determine shear viscosity as a function of shear rate has been successfully applied to predict the viscosity minimum in a bidisperse suspension of colloidal particles at a specific relative volume fraction.

CHAPTER 6
CONCLUSIONS AND FUTURE WORK

The stability of colloidal suspensions depends on the nature of the forces between the particles. In the colloidal size range, Brownian motion, van der Waals attraction, electrostatic repulsion, and steric force interactions are the main forces that need to be considered. In this work, the stability of silica suspensions was manipulated by adding an electrolyte (NaCl) and an adsorbing polymer (PEO). The stability of these aqueous silica/PEO/NaCl suspensions was investigated via time-dependent UV-visible spectrophotometry by varying the PEO concentration and molecular and through the use of two different sample preparation procedures.

Upon "ordered addition" of the PEO and NaCl, a small amount of polymer was effective in preventing the silica particles from flocculating. A higher PEO concentration led to the formation of large flocs that were clearly detectable via size distribution analysis. Rapid settling of the suspension with the higher PEO concentration also occurred. Under "simultaneous addition" of two different PEO molecular weights and NaCl, larger concentrations of polymer were required for steric stabilization. Furthermore, the higher molecular weight polymer appeared to be more effective in stabilizing the silica suspensions in the presence of NaCl, although a lower overall concentration of the polymer was required. This result was probably due to the formation of a denser adsorbed layer for the higher molecular weight PEO. Therefore, in stabilizing silica suspensions at high electrolyte concentrations, the polymer concentration and

molecular weight and the sample preparation procedure all seem to play a role in determining whether or not the suspension will be stable.

When a suspension of colloidal particles is allowed to settle under the influence of gravitational forces, the combined effect of Brownian motion and gravity leads to the phenomena of sedimentation. If the suspension is dilute, theoretical predictions of the sedimentation behavior are feasible. Descriptions of the concentration distribution of the particles as a function of time and vertical distance, under a variety of boundary and initial conditions, are possible.

In this work, an analytical solution was presented as a method to determine time-dependent changes in the concentration of a dilute colloidal suspension at a fixed vertical position. By studying the particle concentration at different fixed positions, the average particle size was determined. Experimental tests were conducted using the UV-visible spectrophotometer, and the results compared reasonable well with the theoretical predictions. Therefore, UV-visible spectrophotometry can serve as a method to characterize the average particle size of a colloidal suspension.

In addition to determining average particle size, in the future UV-visible spectrophotometry may also be used as a tool to determine particle size distribution. It may be possible to de-convolute the time-dependent absorbance curves for a polydisperse suspension to obtain information on the fractions of particle sizes comprising the original suspension. The UV-visible technique is unique in that it incorporates spectroscopy and sedimentation. Algorithms for determining particle size distribution using these two techniques separately have already been proposed [Cummins and Staples (1987);

Shumacher and van de Ven (1991); Chung and Hogg (1985)], and the results are rather encouraging.

The complex rheological behaviors of colloidal suspensions result from colloidal forces, hydrodynamic interactions, particle size distributions, and many other effects. Therefore, the rheological properties of these systems are often studied in order to understand their behavior in relation to a multitude of other phenomena because how the material behaves under shear can play a major role in transport, handling, and processing.

Concentrated monodisperse suspensions and bidisperse suspensions, in which two different size particles are mixed in different proportions, were studied. The shear viscosities of the suspensions were measured using a standard rheological procedure that incorporated time-dependent shear intervals. The standard procedure was developed in order to understand time effects on the shear viscosity. Moreover, it was essential to ensure that the data reported were accurate representations of the rheological behavior of the systems under study since colloidal suspensions have been known to exhibit non-Newtonian flow behaviors and time-dependent rheology.

Under a fixed physicochemical condition, the shear viscosity of a small particle monodisperse suspension was always higher than that of a large particle monodisperse suspension. The behavior occurs because the relative thickness of the electrical double layer is larger for the small particles. For bidisperse suspensions, a minimum in the shear viscosity was observed at a particular value of β (the ratio of the volume fraction of small particles to the total particle volume fraction). This reduction in the shear viscosity upon increasing the degree of suspension polydispersity is apparently associated with microstructural changes in the suspension.

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BIOGRAPHICAL SKETCH

Keisha Michele Wilson was born in Baltimore, MD on April 23, 1972 to Gloria Coles and Kenneth Wilson. She has two younger brothers, Phillip and Kenneth.

After graduating salutatorian of her high school class, Keisha was awarded a full scholarship to attend the University of Maryland at College Park. As an undergraduate, she was inducted into the university Honors Program and Omega Chi Epsilon, the Chemical Engineering Honor Society. She was honored by the Office of Multi-Ethnic Student Education, where she tutored mathematics and chemistry for four years, with an Academic Excellence Award. Keisha held internships with Mobil Research and Development Corporation, Public Service Electric & Gas Company, and Vista Chemical Company, and she was the recipient of the Mobil Foundation Fellowship Award for two consecutive years. Keisha received her Bachelor of Science degree in Chemical Engineering in May of 1995.

In the fall of 1995, Keisha began her graduate studies at the University of Florida. During her years as a graduate student, she received fellowship awards from the Department of Chemical Engineering and the College of Engineering, and she was a National Science Foundation Graduate Minority Fellow. Keisha was also one of the founding members of the first chapter of the National Organization of Black Chemists and Chemical Engineers (NOBCChE) in the state of Florida. The chapter is located on the campus of the University of Florida, and Keisha served as the president and treasurer.

In 1997 and 1998, Keisha worked as a visiting scientist for E. I. du Pont de Nemours and Company in their Particle Science and Technology area. As a result of her outstanding safety and technical performance, she was recognized by DuPont Central Research and Development. Keisha has delivered technical presentations at various locations, including the national meetings of the American Institute of Chemical Engineers (AIChE) and NOBCChE. Keisha is also a certified Engineer Intern.

At the time of writing this work, Keisha had excepted a position as a Research Engineer with E. I. du Pont de Nemours and Company in Wilmington, DE.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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